PB85-156198

# Evaluation of At-Sea Disposal of FGC (Flue Gas Cleaning) Wastes. Volume 2 Biological Testing and Studies with Stabilized Wastes

Little (Arthur D.), Inc., Cambridge, MA

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

Dec 84

U.S. Department of Commerce
National Technical Information Service
NTIS

EPA-600/7-85-001b
December 1984

PB85-156198

# EVALUATION OF AT-SEA DISPOSAL OF FGC WASTES:

# Volume 2. BIOLOGICAL TESTING AND STUDIES WITH STABILIZED WASTES

C.B. Cooper, I. Bodek, C.J. Santhanam

Arthur D. Little, Inc.
Acorn Park
Cambridge, MA 02140

Contract No. 68-03-2334

EPA Project Officer:

Julian W. Jones
Air and Energy Engineering Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

AIR AND ENERGY ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

| TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing) | | |
|---|---|---|
| 1. REPORT NO. EPA-600/7-85-001b | 2. | 3. RECIPIENT'S ACCESSION NO. PB85 156198/AS |
| 4. TITLE AND SUBTITLE Evaluation of At-sea Disposal of FGC Wastes: Vol. 2 Biological Testing and Studies with Stabilized Wastes | | 5. REPORT DATE December 1984<br>6. PERFORMING ORGANIZATION CODE |
| 7. AUTHOR(S) C.B. Cooper, R.R. Lunt, I. Bodek, and C.J. Santhanam | | 8. PERFORMING ORGANIZATION REPORT NO. |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS Arthur D. Little, Inc. Acorn Park Cambridge, Massachusetts 02140 | | 10. PROGRAM ELEMENT NO.<br>11. CONTRACT/GRANT NO. 68-03-2334 |
| 12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Air and Energy Engineering Research Laboratory Research Triangle Park, NC 27711 | | 13. TYPE OF REPORT AND PERIOD COVERED Phase 3, Final: 5/77 - 10/83<br>14. SPONSORING AGENCY CODE EPA/600/13 |

15. SUPPLEMENTARY NOTES AEERL project officer is Julian W. Jones, Mail Drop 61, 919/541-2489. EPA-600/7-77-051 and -600/7-84-005 are related reports (Phases 1 and 2).

16. ABSTRACT This two-part report is the third of a series on a continuing EPA research program on the feasibility of disposing of flue gas cleaning (FGC) wastes in the ocean. Part 1 gives results of laboratory-scale chemical and biological experiments with untreated (unstabilized) FGC wastes designed to provide basic data on environmental impact potential. Part 2 gives results of further chemical and biological tests with a forced-oxidation (sulfate-rich) FGC waste and with stabilized FGC wastes. Results of tests performed to date and related assessment efforts indicate that the conventional (concentrated-dump) at-sea disposal of unstabilized FGC wastes with soil-like properties on the Continental Shelf appears to be environmentally undesirable, unless contradicted by further work. Test results also indicate that at-sea dispersed disposal of sulfate-rich (and, possibly, sulfite-rich) soil-like FGC wastes is sufficiently promising to merit further research. Likewise, results of this and other programs indicate that conventional or concentrated disposal of brick-like stabilized FGC wastes is also promising.

| 17. KEY WORDS AND DOCUMENT ANALYSIS | | |
|---|---|---|
| a. DESCRIPTORS | b. IDENTIFIERS/OPEN ENDED TERMS | c. COSATI Field/Group |
| Pollution<br>Fly Ash<br>Flue Gases<br>Gas Scrubbing<br>Waste Disposal<br>Ocean Environments<br>Assessments | Pollution Control<br>Stationary Sources<br>Flue Gas Cleaning | 13B<br>21B<br>07A, 13H<br><br>08J<br>14B |
| 18. DISTRIBUTION STATEMENT Release to Public | 19. SECURITY CLASS (This Report) Unclassified<br>20. SECURITY CLASS (This page) Unclassified | 21. NO. OF PAGES 90<br>22. PRICE |

EPA Form 2220-1 (9-73)

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

## ABSTRACT - PART TWO

This is Part Two of the third in a series of reports on a research program sponsored by the U.S. Environmental Protection Agency on the feasibility of the disposal of Flue Gas Cleaning (FGC) wastes in the ocean. This part of the report presents the results of laboratory-scale chemical and biological experiments designed to provide basic data on environmental impact potential of at-sea disposal of unstabilized, sulfate-rich, metal-rich FGC wastes and stabilized FGC wastes. The testing was performed by Arthur D. Little, Inc. and the Edgerton Research Laboratory of the New England Aquarium. Part One of the report presents the results of earlier chemical and biological testing with a variety of unstabilized FGC wastes. Results of further investigations of mine disposal of FGC wastes are discussed in a separate report.

The results of testing performed to data and related assessment efforts in this program indicate that dispersed disposal of sulfate-rich (and, possibly, sulfite-rich), soil-like FGC wastes is sufficiently promising to merit further research. Likewise, the results of this and other programs indicate that conventional or concentrated disposal of brick-like stabilized FGC wastes is also promising.

TABLE OF CONTENTS


| | PAGE |
|---|---|
| List of Tables | v |
| List of Figures | vii |
| Acknowledgements | viii |
| Conversion Factors | ix |
| Glossary | x |
| Abbreviations | xi |
| I. SUMMARY | 1 |
| A. Background | 1 |
| B. Purpose and Scope | 4 |
| C. Results | 4 |
| D. Conclusions | 6 |
| E. Recommendations for Additional Research | 7 |
| F. Summary References | 8 |
| II. INTRODUCTION | 9 |
| A. Overview | 9 |
| B. Relationship to Other Studies | 9 |
| C. Purpose and Scope - Part Two | 11 |
| III. CHEMICAL TESTING | 14 |
| A. Introduction | 14 |
| B. Chemical Composition of Waste Samples | 14 |
| C. Sulfite Dissolution and Dissolved Oxygen Depletion Studies for Stabilized Wastes | 20 |
| D. Quiescent Leaching Tests | 28 |

TABLE OF CONTENTS (cont.)


| | PAGE |
|---|---|
| IV. BIOLOGICAL TESTING | 47 |
| A. Experimental Design | 47 |
| B. Results and Discussion | 49 |
| V. SUMMARY EVALUATION OF ENVIRONMENTAL IMPACT POTENTIALS | 68 |
| A. Benthic Sedimentation Impacts | 68 |
| B. Suspended Sediment Impacts | 69 |
| C. Sulfite-Related Oxygen Depletion | 69 |
| D. Trace Contaminant Impacts | 70 |
| VI. CONCLUSIONS | 72 |
| VII. RECOMMENDATIONS FOR ADDITIONAL RESEARCH | 74 |
| VIII. REFERENCES | 75 |

## LIST OF TABLES


| | | PAGE |
|---|---|---|
| TABLE 1 | DISTRIBUTION OF TESTS PERFORMED ON VARIOUS SAMPLES (PART II) | 15 |
| TABLE 2 | SUMMARY OF FGD WASTES ANALYSES (SCREENING DATA) | 17 |
| TABLE 3 | COMPARISON OF CONCENTRATIONS OF ELEMENTS IN FGC WASTES | 18 |
| TABLE 4 | MAJOR AND TRACE CHEMICAL COMPOSITION OF WASTE SAMPLES | 21 |
| TABLE 5 | DISSOLUTION DATA FOR STABILIZED SULFITE-RICH WASTES IN SEAWATER | 25 |
| TABLE 6 | APPARENT SOLUBILITY PRODUCT FOR CALCIUM SULFITE IN SEAWATER | 26 |
| TABLE 7 | CUMULATIVE AMOUNT OF TRACE METALS RELEASED PER TIME FOR FORCED OXIDATION AND STABILIZED WASTES IN MICROGRAMS | 30 |
| TABLE 8 | CUMULATIVE AMOUNT OF TRACE METALS RELEASED PER TIME FOR FORCED OXIDATION AND STABILIZED WASTES IN MICROGRAMS | 31 |
| TABLE 9 | CUMULATIVE AMOUNT OF TRACE METALS RELEASED PER TIME FOR FORCED OXIDATION AND STABILIZED WASTES IN MICROGRAMS | 32 |
| TABLE 10 | CUMULATIVE AMOUNT OF TRACE METALS RELEASED PER TIME FOR FORCED OXIDATION AND STABILIZED WASTES IN MICROGRAMS | 33 |
| TABLE 11 | CUMULATIVE AMOUNT OF TRACE METALS RELEASED PER TIME FOR FORCED OXIDATION AND STABILIZED WASTES IN MICROGRAMS | 34 |
| TABLE 12 | TOTAL AMOUNT OF TRACE ELEMENTS PRESENT IN BACKGROUND TANK | 35 |
| TABLE 13 | STABILITY OF TRACE ELEMENTS IN SEAWATER TANK | 36 |
| TABLE 14 | CUMULATIVE AMOUNT OF TRACE ELEMENTS LEACHED INTO SEAWATER | 41 |
| TABLE 15 | TRACE ELEMENTS LEACHED FROM SULFATE-RICH, UNSTABILIZED FGD WASTES INTO SEAWATER: A COMPARISON OF RESULTS FROM 1978 AND 1982 | 46 |

LIST OF TABLES (cont.)


| | | PAGE |
|---|---|---|
| TABLE 16 | TRACE ELEMENT CONCENTRATIONS IN SEAWATER FOR QUIESCENT LEACHING TESTS AND FOR LONG-TERM BIOASSAY TESTS | 50 |
| TABLE 17 | MORTALITIES OCCURING DURING THE BIOCONCENTRATION STUDY | 51 |

## LIST OF FIGURES


| | | PAGE |
|---|---|---|
| FIGURE 1 | DISSOLVED OXYGEN DEPLETION RATES | 22 |
| FIGURE 2 | SULFITE DISSOLUTION RATES | 27 |
| FIGURE 3 | CADMIUM RELEASE | 37 |
| FIGURE 4 | SELENIUM RELEASE | 38 |
| FIGURE 5 | ARSENIC RELEASE | 39 |
| FIGURE 6 | CHROMIUM RELEASE | 40 |
| FIGURE 7 | ARSENIC ACCUMULATION IN LITTORINA | 53 |
| FIGURE 8a | ARSENIC ACCUMULATION IN NEREIS | 54 |
| FIGURE 8b | ARSENIC ACCUMULATION IN MYA | 54 |
| FIGURE 9 | ARSENIC IN WASTES, WATER COLUMN AND ORGANISM TISSUE | 55 |
| FIGURE 10a | CADMIUM ACCUMULATION IN LITTORINA | 56 |
| FIGURE 10b | CADMIUM ACCUMULATION IN NEREIS | 57 |
| FIGURE 10c | CADMIUM ACCUMULATION IN MYA | 57 |
| FIGURE 11 | CADMIUM IN WASTES, WATER COLUMN AND ORGANISM TISSUE | 58 |
| FIGURE 12a | CHROMIUM ACCUMULATION IN LITTORINA | 60 |
| FIGURE 12b | CHROMIUM ACCUMULATION IN NEREIS | 62 |
| FIGURE 12c | CHROMIUM ACCUMULATION IN MYA | 62 |
| FIGURE 13 | CHROMIUM IN WASTES, WATER COLUMN AND ORGANISM TISSUE | 63 |
| FIGURE 14a | SELENIUM ACCUMULATION IN LITTORINA | 64 |
| FIGURE 14b | SELENIUM ACCUMULATION IN NEREIS | 65 |
| FIGURE 14c | SELENIUM ACCUMULATION IN MYA | 65 |
| FIGURE 15 | SELENIUM IN WASTES, WATER COLUMN AND ORGANISM TISSUE | 66 |

## ACKNOWLEDGEMENTS - PART TWO

This study was conducted by Arthur D. Little, Inc. for the U.S. Environmental Protection Agency under Contract No. 68-03-2334, and by the Edgerton Research Laboratory of the New England Aquarium under EPA Grant No. R805654010.

This report reflects the work of many members of Arthur D. Little, Inc. and the NEA staff. Those participating in this phase of the program are listed below.

| Arthur D. Little, Inc. | Edgerton Research Laboratory<br>New England Aquarium |
|---|---|
| **Principal Investigators:** | |
| C.J. Santhanam, Project Manager | A.J. Barker, Director, Research |
| C.B. Cooper | B.A. Penney |
| I. Bodek | K.A. Smith |
| | D.K. Ryan |
| | D. Ofer |
| **Contributing Staff:** | |
| M. Rossetti | T.J. Coffey |
| A.C. Roche | M.P.J. Kaltofen |
| | D. Elwood |
| | T.R. Gilbert |

Many other individuals and organizations have made contributions to this study. In particular, we wish to acknowledge the continuing assistance and guidance provided by Julian W. Jones, the EPA Project Officer. We would also like to thank the utility companies which supplied FGC waste samples used in the testing.

## CONVERSION FACTORS

| English/American Units | Metric Equivalent |
|---|---|
| **Length:** | |
| 1 inch | 2.540 centimeters |
| 1 foot | 0.3048 meters |
| 1 fathom | 1.829 meters |
| 1 mile (statute) | 1.609 kilometers |
| 1 mile (nautical) | 1.852 kilometers |
| **Area:** | |
| 1 square foot | 0.0929 square meters |
| 1 acre | 4,047 square meters |
| **Volume:** | |
| 1 cubic foot | 28.316 liters |
| 1 cubic yard | 0.7641 cubic meters |
| 1 gallon | 3.785 liters |
| **Weight/Mass:** | |
| 1 pound | 0.4536 kilograms |
| 1 ton (short) | 0.9072 metric tons |
| **Pressure:** | |
| 1 pound per square inch | 0.07031 kilograms per square centimeter |
| **Concentration:** | |
| 1 part per million (weight) | 1 milligram per liter |
| **Speed:** | |
| 1 knot | 1.853 kilometers per hour |
| **Energy/Power:** | |
| 1 British Thermal Unit | 1,054.8 joules |
| 1 megawatt | $3.600 \times 10^9$ joules per hour |
| **$\Delta$ Temperature:** | |
| 1 degree Fahrenheit | 5/9 degree Centrigrade |

## GLOSSARY

Cementitious: A chemically precipitated binding of particles resulting in the formation of a solid mass.

Fixation: The process of putting into a stable or unalterable form.

Impoundment: Reservoir, pond, or area used to retain, confine, or accumulate a fluid material.

Leachate: Soluble constituents removed from a substance by the action of a percolating liquid.

Leaching Agent: A liquid used to percolate through a substance that results in the leaching of soluble constituents.

Pozzolan: A siliceous or aluminosiliceous material that in itself possess little or no cementitious value but that in finely divided form and in the presence of moisture will react with alkali or alkaline earth hydroxide to form compounds possessing cementitious properties.

Pozzolanic Reaction: A reaction producing a pozzolanic product.

Stabilization: Making stable by physical or chemical treatment.

Reproduced from best available copy.

## ABBREVIATIONS

| | |
|---|---|
| Btu | British thermal unit |
| cm | centimeter |
| cm/sec | centimeter per second |
| $^{o}C$ | degrees Centigrade |
| $^{o}F$ | degrees Fahrenheit |
| ESP | electrostatic precipitator |
| FGC | flue gas cleaning |
| FGD | flue gas desulfurization |
| ft | feet |
| ft/sec | feet per second |
| g | gram |
| gal | gallon |
| gpm | gallons per minute |
| hp | horsepower |
| hr | hour |
| in. | inch |
| j | joule |
| j/s | joule per second |
| k | thousand |
| kg | kilogram |
| km | kilometer |
| kW | kilowatt |
| kWh | kilowatthour |
| l | liter |
| lb | pound |
| M | million |
| $m^2$ | square meter |
| $m^3$ | cubic meter |
| Mw | megawatt |
| ppm | parts per million |
| psi | pounds per square inch |
| sec | second |
| TDS | total dissolved solids |

**Note: For conversion units, see page ix.**

# I. SUMMARY

## A. Background

This is Part Two of the third in a series of reports on a research program sponsored by the U.S. Environmental Protection Agency on the feasibility of disposal of Flue-Gas Cleaning (FGC) wastes from coal-fired power plants in mines and at sea. The previous two reports (1)(2) presented findings concerning both mine and ocean disposal. The initial study (1) consisted of issue identification for future research, based on review of available information. The report on the second phase of work (2) included the results of original physical and chemical testing as well as additional assessment of available information. This report, presented in two parts, describes the subsequent investigations of ocean disposal by Arthur D. Little, Inc. (ADL) and the Edgerton Research Laboratory of the New England Aquarium (NEA). A separate report covers the further investigations of mine disposal.

Initial studies in this program (1) identified four environmental impact categories of concern in the potential at-sea disposal of FGC wastes from coal-fired power plants. These categories were:

- benthic sedimentation;
- suspended waste in the water column;
- sulfite-related toxicity and oxygen depletion; and
- trace contaminants.

The second phase of the program (2) focused on physical and chemical investigations of unstabilized FGC wastes in seawater. Testing and assessment efforts emphasized three subject areas:

- physical fate of unstabilized FGC wastes in the water column;

- physical fate of unstabilized FGC wastes on the ocean bottom; and

- chemical fate of unstabilized FGC wastes in seawater.

Overall conclusions of the first two phases emphasized the need for case-by-case analyses of prospective at-sea disposal of FGC wastes and the viability of available control options, along with the following more specific conclusions:

- The conventional disposal of unstabilized FGC wastes with soil-like physical properties on the continental shelf appeared to be environmentally undesirable without further contradictory evidence.

- Problems of at-sea disposal of sulfite-rich FGC wastes, particularly those related to oxygen depletion, appeared to be much greater than the problems associated with other FGC wastes.

- Disposal options which appeared promising and worthy of further research included:

  - dispersed disposal of unstabilized, sulfate-rich and stabilized, brick-like FGC wastes on the continental shelf;

  - concentrated disposal of brick-like FGC wastes; and

  - disposal of unstabilized, sulfate-rich FGC wastes in the deep ocean.

In Part One of this third phase of study, experiments were designed to investigate:

1. acute toxicity of unstabilized FGC wastes to marine water column organisms;

2. chronic toxicity and substrate suitability of unstabilized FGC wastes for marine benthic organisms; and

3. leaching behaviors and bioaccumulation of trace contaminants from FGC wastes in seawater.

The Part One results generally reaffirmed the earlier conclusions cited above and led to the following additional conclusions:

- Dispersed disposal appeared to be a potentially useful control option for mitigating the problems of disposal of sulfite-rich FGC wastes.

- The potential release of some trace contaminants remained a valid concern that could preclude at-sea disposal of certain FGC wastes. This concern did not appear to extend to nickel and zinc.

- Dispersed disposal at-sea of all forms of FGC wastes and concentrated disposal of stabilized, brick-like FGC wastes appeared promising and were recommended for further research.

- Conventional disposal of unstabilized, sulfate-rich FGC wastes in the deep ocean may be promising, but needed to be reconsidered after further testing to determine if the toxicity of one such waste in the program was an isolated phenomenon.

The five research needs identified at the conclusion of Part One were:

- further bioassay data on sulfate-rich FGC wastes;

- further leaching and bioassay data on selected FGC waste trace contaminants;

- limited field-scale tests to investigate avoidance responses and trace contaminant uptake;

- parallel data for stabilized FGC wastes; and

- continued investigations of any full-scale field situations where FGC wastes have entered or been placed in marine environments.

## B. Purpose and Scope

Three of the research needs identified in the Part One study were addressed in Part Two of the study. These needs were:

1. Development of further bioassay data on a type of unstabilized sulfate-rich FGC waste that had been associated with high levels of organism mortality in previous testing;

2. Development of further leaching and bioassay data on selected FGC waste trace metals in seawater; and

3. Development of chemical and bioassay data parallel to that from earlier studies, this time for a representative selection of stabilized FGC wastes.

## C. Results

### 1. Benthic Sedimentation Impacts

The results of the Part Two thirty-day exposure tests with both unstabilized and stabilized, soil-like FGC wastes included observations of voluntary use (in some cases preferential) of these wastes as substrates by facultative, benthic marine organisms which would otherwise inhabit various or fine-grained natural substrates (i.e., clams and worms). No examples of waste avoidance by these organisms were observed. These observations tend to indicate that the physical characteristics of soil-like FGC wastes are compatible with use by facultative marine organisms at dumpsites set in other fine-grained sediments. However, there are still no data to contradict

the expectation that fine-grained, soil-like FGC wastes would prove unsuitable substrate for indigenous organisms if concentrated on areas of the ocean bottom that would otherwise be covered by coarse sand and/or reef substrates.

2. Sulfite-Related Oxygen Depletion

The investigation of oxygen depletion by sulfite-rich stabilized wastes in Part Two of this study indicated that such depletion would occur with these wastes, but to a lesser degree and at a slower rate than previously measured for unstabilized, sulfite-rich wastes (2). Higher slurry concentrations of stabilized versus unstabilized wastes were required to produce oxygen depletion, and the time required to deplete the available oxygen increased by factors of about two to five, even at the higher slurry concentrations. No oxygen depletion below 5.8 ppm was experienced in any of the thirty-day exposure tests with sulfite-rich, stabilized wastes. However, the wastes were not subjected to the same degree of bio-turbation in the Part Two tests that had prevailed and proved problematic in Part One of the study.

3. Trace Contaminant Impacts

The results of the leaching and biological exposure testing in Part Two of the study tended to confirm for additional stabilized and unstabilized FGC wastes the Part One findings with respect to nickel and zinc, and to indicate leaching behavior and implications similar to those for nickel and zinc with respect to copper. For all three of these metals, the incremental changes in ambient seawater concentrations were below the levels reported to cause adverse ecological effects in the marine environment (3)(4)(5)(6), and in some cases resulted in net decrease over background levels.

There were no apparent waste-related test organism mortalities in the Part Two tests. These results, particularly for the two wastes that were physically and chemically comparable the toxic sample of sulfate-rich unstabilized wastes used in Part One, tend to reinforce

the hypothesis that the toxicity of that sample in Part One was a relatively unique phenomenon.

Results for other trace metals, notably arsenic, cadmium, chromium, and selenium, were inconclusive. There was an absence of apparent toxicity and environmentally significant bioaccumulation of these elements over the thirty-day exposure period in the Part Two tests. However, the concentrations of these elements were continuing to rise in one or more test species at the conclusion of the tests.

Stabilization appeared to reduce the availability of cadmium for seawater leaching, but appeared to have little or no effect on the availability of other elements, including chromium and selenium.

## D. Conclusions

Principal conclusions of this part of the study were as follows:

- The two overall conclusions of the earlier assessments (1)(2) are still considered valid.

- The at-sea disposal of stabilized, sulfite-rich FGC waste appears to be environmentally preferable from the standpoint of sulfite-related oxygen depletion. Mitigation by dispersed disposal may be feasible and necessary, but requires field-scale investigation.

- The previously observed incidence of contamination-related acute or sub-chronic toxicity associated with one sample of a sulfate-rich, unstabilized FGC wastes appears to have been highly waste-specific. Such toxicity should not be expected for a broad spectrum of sulfate-rich FGC wastes, and can be evaluated on a case-by-case basis with required, standard ocean disposal bioassays.

- The limited potential for near-term release and accumulation of copper, nickel and zinc from either unstabilized or stabilized FGC wastes appears unlikely to constrain at-sea disposal of these wastes.

- The data suggest that leaching of As, Cd, Cr and Se appears to be within environmentally acceptable limits for relatively short-term exposures, but leave open some questions about the impacts of prolonged exposure.

- FGC waste stabilization by addition of lime and fly ash appears to be a potentially effective means of mitigating impacts associated with the release of some trace metals (e.g., Cd) but not others (e.g., Se, Cr).

- Disposal options which continue to appear promising and are recommended for further research include:

  - dispersed disposal of all forms of FGC wastes on the continental shelf or in the deep ocean;

  - conventional or concentrated disposal of stabilized FGC wastes on the continental shelf or in the deep ocean; and

  - conventional or concentrated disposal of unstabilized, sulfate-rich FGC wastes in the deep ocean.

## E. Recommendations for Additional Research

The following research needs were identified based on Part Two of the study:

- Limited field-scale tests with sulfite-rich and metal-rich FGC wastes should be conducted to investigate the importance of:

1. organism avoidance responses as potentially mitigative of sulfite-related toxicity of sulfite-rich FGC wastes; and

2. longer-term chronic uptake and toxicity of As, Cd, Cr and Se leached from FGC wastes under more representative conditions for leaching and water exchange.

- o Investigation of any field situations where FGC wastes have entered or been placed in marine environments should be encouraged.

## F. References


1. Lunt, R.R., C.B. Cooper, S.L. Johnson, J.E. Oberholtzer, G.R. Shimke, and W.I. Watson, "An Evaluation of the Disposal of Flue Gas Desulfurization Wastes in Mines and the Ocean: Initial Assessment," EPA 600/7-77-051, U.S. Environmental Protection Agency, Office of Research and Development, 1977.

2. Lunt, R.R., C.B. Cooper, A.S. Reyman, S.L. Johnson, I. Bodek, W.I. Watson (Arthur D. Little, Inc.) and G.C. McLeod, A.J. Barker (Edgerton Research Laboratory, New England Aquarium), "An Evaluation of the Disposal of Flue Gas Desulfurization Wastes in Coal Mines and At-Sea: Refined Assessment," U.S. Environmental Protection Agency, Office of Research and Development, Contract No. 68-03-2334, 1981.

3. Federal Register, Volume 44, No. 52, March 15, 1979.

4. Eisler, Ronald and Raymond J. Hennekey, "Acute Toxicities of $Cd^{2+}$, $Cr^{+6}$, $Hg^{2+}$, $Ni^{2+}$ and $Zn^{+2}$ to Estuarine Macrofauna," EPA-600/J-77-151, U.S. Environmental Protection Agency, Environmental Research Laboratory, Narragansett, Rhode Island, 1977.

5. Eisler, Ronald, Trace Metal Concentrations in Marine Organisms, Pergamon Press, 1981.

6. Eisler, Ronald and Raymond J. Hennekey, "Toxicity Evaluation of a Complex Metal Mixture to the Soft Shell Clam (Mya arenaria)," EPA-600/J-77-149, U.S. Environmental Protection Agency, Environmental Research Laboratory, Narragansett, Rhode Island, 1977.

## II. INTRODUCTION

### A. Overview

This is Part Two of the third in a series of reports on a research program sponsored by the Industrial Environmental Research Laboratory of the U.S. Environmental Protection Agency. The program involves investigations of disposal in mines and in the ocean of flue-gas cleaning (FGC) wastes from utility coal combustion. Previous reports in this series include an initial assessment (1) and a refined assessment (3), which reported findings (summarized in Part One of this report) concerning both mine and ocean disposal. This report presents the results of further investigations of ocean disposal of FGC wastes in two parts. Part One describes the results of aquatic toxicity testing with unstabilized (untreated) FGC wastes and marine organisms. This part (Part Two) describes the results of chemical and biological testing with stabilized (treated) FGC wastes and additional toxicity testing with two metal-rich unstabilized FGC wastes. The findings of further investigations of mine disposal of FGC wastes are to be reported separately.

### B. Relationship to Other Studies

During the timeframe of the investigations reported in this series, investigations of ocean disposal of stabilized FGC wastes continued at the State University of New York (S.U.N.Y.), Stonybrook, under the sponsorship of various agencies. The S.U.N.Y. work involves a series of laboratory and limited field-scale studies of the physical and chemical characteristics and ecological impact potential of "artificial reefs" made of brick-like, sulfite-rich FGC wastes stabilized by a modified version of the Conversion Systems Inc. (CSI) process. This work collectively referred to as the Coal-Waste Artificial Reef Program (C-WARP) is reported in references (10, 11 and 12).

The investigators for this study maintained cognizance of the S.U.N.Y. work, and attempted to design their experiments so as to complement,

rather than duplicate that work. In particular, Part Two of this program focused on the study of soil-like (rather than brick-like) stabilized FGC wastes, and sulfate-rich (forced-oxidation) wastes, neither or which were studied by S.U.N.Y. However, some of the S.U.N.Y. results concern subjects of common interest to the investigators in both programs, and are discussed here as additional background to Part Two of this report.

One of the principal impact issues identified in previous reports in this series (1) and (2) and in Part One of this report is the phenomenon of sulfite-related oxygen depletion observed upon placement of sulfite-rich FGC wastes in seawater. The S.U.N.Y. C-WARP studies provide an additional perspective on this issue because they involved placement and observation of brick-like, stabilized, sulfite-rich FGC wastes in a small bay and in the ocean. The C-WARP wastes did not produce any toxic oxygen-depletion phenomena at field-scale in either the bay or ocean environments. Because of their brick-like nature, these wastes have not been subject to the type of bio-turbation that resulted in the dramatic oxygen depletion and toxicity described for an unstabilized, sulfite-rich waste in Part One of this report. Additionally, finfish and other marine life have continued to inhabit the immediate vicinity of the C-WARP wastes for several months in both bay and ocean environments, indicating that no significant oxygen depletion is occurring in the absence of bio-turbation.(11)(12)

Consistent with the S.U.N.Y. investigators' overall conclusions that it is too early to judge beneficial or adverse effects(12), it is too early to tell what the ultimate structural integrity of the C-WARP wastes will be, and whether, if an when they lose their structural integrity, these wastes would have significant oxygen depletion potential. Additionally, these observations do not address the oxygen depletion potential of soil-like FGC wastes.

The S.U.N.Y. investigators made observations that relate to the suitability of brick-like, stabilized wastes as benthic substrates. In several months of observations at both bay and ocean sites, the

investigators documented levels of organism growth on and use of the stabilized FGC wastes that was generally comparable in magnitude and diversity to that observed on two other types of "control" substrates - concrete blocks and natural hard rock (10)(11)(12). Again, these findings do not specifically address the basic issue of suitability of the many soil-like FGC wastes as benthic substrates, but they do indicate that brick-like forms of stabilized wastes have the physical characteristics to attract and support marine organisms in a manner analagous to other elevated, relatively hard structures on the ocean floor.

The S.U.N.Y. investigators also performed and reported laboratory studies of various physical, chemical and biological impact issues that can be considered more uniquely associated with the special nature of the stabilized, brick-like wastes than with the broader impact issues identified in the earlier phases of the program reported here. For example, the C-WARP program reports (10)(11)(12) present the results of strength testing, analyses of waste chemical composition and dissolution behavior, and acute toxicity and metals bioaccumulation tests with ground slurries of the stabilized, brick-like wastes. In each case, the experimental design and/or results are independently valuable, but are sufficiently unique so as to provide no significant additional background information for interpretation of the results of Parts One and Two reported here.

## C. Purpose and Scope - Part Two

Based on the findings described in Part One of this report and an awareness of the scope of ongoing work at S.U.N.Y., a program was defined to address three of the five more important research needs identified at the end of Part One. These needs addressed were as follows:

1. Development of further bioassay data on the type of unstabilized, sulfate-rich FGC waste that had been associated with high levels of organism mortality in the previous testing;

2. Development of further leaching and bioassay data on selected trace metals (arsenic, selenium, copper, cadmium and chromium) in FGC wastes; and

3. Development of chemical and bioassay data parallel to that from the earlier studies in this program, this time for a representative selection of stabilized FGC wastes.

The scope of the activities covered in this part of the report includes:

- screening and selection for further testing of unstabilized FGC wastes having relatively high concentrations of the selected trace metals and comparable to the waste previously associated with unusually high toxicity in the Part One test program;

- chemical characterization of these unstabilized FGC wastes and a variety of stabilized FGC wastes;

- characterization of the sulfite dissolution and oxidation behavior of several sulfite-rich, stabilized FGC wastes in seawater;

- characterization of the trace metal leaching behavior of the additional unstabilized and stabilized FGC wastes in seawater; and

- bioassay testing involving thirty-day exposure of several marine invertebrates to the additional unstabilized and stabilized FGC wastes.

The screening, major species characterization and dissolution/oxidation work above was carried out by Arthur D. Little, Inc. (ADL) under EPA Contract No. 68-03-2334. The trace metal characterization, leaching experiments and bioassay testing were performed by the Edgerton Research Laboratory of the New England Aquarium (NEA) under EPA

Research Grant No. R805654010. The results of these investigations are described below in separate sections on chemical and biological testing.

## III. CHEMICAL TESTING

### A. Introduction

This section describes the chemical and leaching properties of the selected forced oxidation and stabilized FGD waste materials used in Part Two of the study. The properties described include major and trace chemical composition, rate of dissolution of sulfite from the wastes into seawater, rate of depletion of oxygen in seawater by the presence of sulfite in the waste and rates of leaching of selected trace components from the wastes into seawater under quiescent (non-stirred) contact conditions. Where feasible, a comparison of results obtained in Part One of this study under similar experimental conditions to those in this part is presented.

A summary of the waste samples used in this part of the study and the distribution of the various tests performed using the particular samples are provided in Table 1.

### B. Chemical Composition of Waste Samples

#### 1. Screening and Selection of Trace Metal Rich Unstabilized Waste Samples

In order to select waste samples that would represent FGC wastes containing relatively high concentrations of the trace elements found to be of interest in the preceding phase of this program (e.g., Cr, Cu, Cd, Se, Ni, Zn), samples of wastes from a variety of FGC processes were subjected to multi-element chemical analysis using Inductively Coupled Argon Plasma Spectroscopy (ICAP)[a]. The samples were totally digested using a mixture of $HF/HNO_3/H_2SO_4$ acids prior to analysis . Samples with and without ash from a variety of scrubbing processes were

[a] ICAP analyses and digestions were performed by Barringer Magenta Ltd., Toronto, Ontario, Canada.

TABLE 1

Distribution of Tests Performed on Various Samples (Part II)

| Sample[a] | Major Component Characterizations | Trace Element Characterizations[b] | ICAP[c] | TOS Dissolution[d] | Quiescent Leaching[e] | Long-Term Exposure[e] |
|---|---|---|---|---|---|---|
| ST1 | | ✓ | | ✓ | | |
| ST2 | ✓ | ✓ | | ✓ | ✓ | ✓ |
| ST3 | ✓ | ✓ | | ✓ | ✓ | ✓ |
| FO1 | ✓ | ✓ | ✓ | | ✓ | ✓ |
| FO2 | ✓ | ✓ | ✓ | | ✓ | ✓ |
| ST4 | ✓ | ✓ | | | ✓ | ✓ |

[a] ST1 - a sulfite-rich FGD waste stabilized using lime and flyash addition.
ST2 - similar to ST1.
ST3 - similar to ST1.
FO1 - a sulfate-rich forced oxidation FGD waste.
FO2 - a sulfate-rich flyash scrubbing FGD waste.
ST4 - a sulfate-rich forced oxidation FGD waste stabilized by addition of lime.

[b] Analysis for As, Cd, Sr, Cu, Ni, Se, Zn (performed at New England Aquarium).

[c] Analysis for Al, Ca, Fe, K, Mg, Na, Ti, Be, Cr, Cu, Mn, Ni, Pb, V, Zn, P, Sr, Zr, Ag, Co, Mo, Tl (Barringer Magenta Ltd).

[d] Performed at Arthur D. Little, Inc.

[e] Performed at New England Aquarium.

[f] Analysis for Ca, total oxidizable sulfur, sulfate, acid insolubles, % solids and slurry pH. Performed at Arthur D. Little, Inc.

Source: Arthur D. Little, Inc.

analyzed. The concentrations observed for the various elements in these wastes are summarized in Table 2.

In general, as expected, due to the higher concentration of certain major components (e.g., Al, Fe, K, Ti) in the ash versus FGD fractions of the wastes, these elements were present at higher concentrations in FGD samples containing ash than in those which did not. Similar trends were also observed for many trace components (e.g., Be, Cr, Cu, Ni, Pb, V, Zr). The samples containing ash had a lower Ca content, as expected, since FGD wastes contain as a major component Ca and thus the presence of ash in effect dilutes the Ca content.

With regard to certain trace elements of concern in this study (Cr, Cu, Ni and Zn), the initial screening analysis suggested that samples 2 and 5 (subsequently referred to as FO2 and FO1, respectively) would represent samples containing concentrations in the upper end of the range observed in the available samples. Sample FO1 was a forced oxidation sulfate-rich sample from a limestone scrubbing process. Sample FO2 was a sulfate-rich sample from a fly ash scrubbing process. Table 3 provides a comparison of the trace composition of interest in this study in these samples to those reported for a larger number of FGD waste samples from other studies (2) and compared to all the samples screened in this part of the work. This table indicates that the FO1 and FO2 samples would represent the upper range in concentration for the reported elements. In addition, sample FO1 was produced by the same system (at the same plant but in a different time period) that produced the LS-3 waste that proved highly toxic in the exposure testing work described in Part One of this report.

## 2. Preparation and Source of Stabilized Waste Samples

In order to assess the effect of stabilization both on the leaching rates of the selected trace components and on organism exposure, samples of sulfite and sulfate-rich stabilized wastes were utilized. Samples of sulfite-rich stabilized FGC wastes were provided by the State University of New York (S.U.N.Y.), sample ST1 and by the operator

TABLE 2

Summary of FGD Waste Analyses (Screening Data)

| Sample | FGD Process | Major Components (%) Al | Ca | Fe | K | Mg | Na | Ti | Trace Components (ppm)[a] Be | Cr | Cu | Mn | Ni | Pb | V | Zn | P | Sr | Zr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| FGD Without Ash: | | | | | | | | | | | | | | | | | | | |
| 1 | Lime | 0.77 | 31.1 | 0.47 | 0.03 | 0.17 | 0.06 | 0.03 | <0.05 | 2.2 | 8.4 | 46 | 12 | <5 | 6.5 | 14 | 70 | <0.1 | 14 |
| 3 | Limestone | 0.36 | 32.3 | 0.19 | 0.13 | 0.42 | 0.62 | 0.003 | <0.05 | 6.8 | 3.5 | 661 | <2 | <5 | <0.5 | 2160 | 450 | 26 | 9.6 |
| 4 | Limestone | 0.69 | 28.5 | 0.13 | 0.06 | 0.39 | 0.30 | 0.04 | <0.05 | 8.1 | 3.3 | 10 | <2 | 5 | 4.5 | <1 | 340 | <16 | 25 |
| 9 | Limestone | 0.32 | 33.5 | 0.13 | 0.08 | 0.06 | 0.28 | 0.008 | <0.05 | <0.8 | 1.5 | 13 | <2 | <5 | <0.5 | 923 | 90 | 18 | 9.1 |
| FGD With Ash: | | | | | | | | | | | | | | | | | | | |
| 5 | (F01)[c] Forced Oxidation | 4.79 | 18.2 | 2.96 | 1.09 | 0.33 | 0.60 | 0.26 | 2.16 | 34 | 34 | 111 | 54 | 40 | 104 | 358 | 340 | 169 | 106 |
| 2 | (F02)[c] Alkaline Ash | 7.93 | 21.4 | 2.23 | 0.68 | 0.61 | 0.66 | 0.38 | 2.22 | 87 | 55 | 764 | 18 | 35 | 74 | 16 | 520 | 2580 | 190 |
| 6 | Limestone | 3.17 | 10.0 | 3.90 | 0.70 | 0.48 | 0.17 | 0.18 | 1.84 | 14 | 21 | 131 | 32 | 30 | 174 | 189 | 160 | 255 | 58 |
| 7 | Fly Ash Scrubbing | 5.85 | 8.74 | 5.66 | 1.05 | 0.36 | 1.64 | 0.32 | 2.93 | 78 | 106 | 352 | 36 | 40 | 137 | 91 | 140 | 65 | 173 |
| 8 | Carbide Lime Process | 1.21 | 29.1 | 0.98 | 0.16 | 0.29 | 0.74 | 0.06 | <0.05 | 8.9 | 21 | 77 | 13 | 5 | 28 | 30 | 60 | <0.1 | 27 |

a Data for Ag, Co, Mo and Th were below detection limits for all samples (<.05, <5, <30, <1 ppm, respectively). Data for Cd was rejected due to the unacceptability of the quality control results. Analysis was performed using Inductively Coupled Argon Plasma Emission Spectroscopy.
b Low recovery of standard (46%) makes absolute values questionable. Data may be useful in comparing wastes.
c Samples used in subsequent experiments in this part of the study.

Source: Arthur D. Little, Inc.



Reproduced from best available copy.

TABLE 3

Comparison of Concentrations of Elements in FGD Wastes[a]

| Element | Sample FO1 | Sample FO2 | Range for Analyzed Samples[b] | Literature Reported Range[c] |
|---|---|---|---|---|
| Cr | 34 | 87 | <0.8 - 87 | 2-250 |
| Cu | 34 | 55 | 1.5 - 106 | 1-76 |
| Ni | 54 | 18 | <2 - 54 | 6-27 |
| Zn | 358 | 16 | <1 - 2160 | 10-320 |

[a] All data in ppm
[b] This study
[c] Ref 2

of two full scale waste disposal sites which utilize fly ash and lime addition in the Conversion Systems Inc. (CSI) stabilization process (samples ST2 and ST3). The latter two samples were obtained in small boulder-size pieces and were used in subsequent experiments (see Table 1). Sample ST1 (a single block) was only analyzed for trace components and sulfite dissolution rates in order to determine difference between that laboratory-prepared sample and the samples obtained from the field.

Since no full-scale or small-scale desulfurization processes currently involves stabilization of sulfate-rich forced oxidation wastes, stabilized samples were prepared in the laboratory by addition of lime. This sample (ST4) was prepared by addition of 2% by weight of hydrated lime (reagent grade) and 10% by weight of water to the unstabilized forced oxidation sample, FO1. The initial moisture content of FO1 was 20% and it contained 40% fly ash (measured as acid insoluble material). The ingredients were mixed thoroughly in a large blender and placed into two wooden drawers lined with polyethylene. The mixed ingredients were placed in the box using very light compaction. The drawers were then covered and allowed to sit at room temperature for a period of 45 days. One sample (40 cm x 50 cm x 5 cm) was prepared for the quiescent leaching tests and another (25 cm x 40 cm x 5 cm) for the thirty-day organism exposure tests.

The progress of the reaction was determined by titration of samples with 0.1 N HCl to pH 7. The initial calculated alkalinity of the mixture based on addition of 2% lime should have been about 0.54 mmoles $OH^-$/gram. After 14 days, the hydroxide content was 0.14 mmoles/gram and after 45 days (when the sample was provided to the New England Aquarium) the value was 0.04 mmoles per gram. The pH of a 10% slurry of the stabilized mix after 45 days curing was 10.2.

The resultant cured material, although produced with minimal compaction, was more cohesive than the stabilized sulfite materials ST2 and ST3 and did not powder readily (see Appendix).

### 3. Chemical Composition of Waste Samples Studied

The major and trace chemical composition of unstabilized and stabilized samples used in this part of the study are provided in Table 4. For comparison data are also provided for samples of unstabilized waste used in Part One of this study (samples DA1, L1 and LS3). As these data show, the samples used in this part of the study are comparable in major and trace composition to those of the first part (comparing stabilized and unstabilized sulfate-rich and sulfite-rich separately) for the trace elements analyzed.

## C. Sulfite Dissolution and Dissolved Oxygen Depletion Studies for Stabilized Wastes

In order to address the effect of lime/fly ash stabilization on the availability and effect of sulfite released from the wastes into the seawater environment, two principal experimental comparisons were made with previous experiments performed on unstabilized sulfite-rich FGC wastes in the Part One studies. These experiments were: measurement of the rate of dissolution and equilibrium concentration of $CaSO_3$ in seawater and measurement of the rate of depletion of dissolved oxygen in seawater by the presence of dissolved species from the wastes. The procedures used to perform these experiments and the methods used to determine concentrations of sulfite, calcium, and dissolved oxygen were described previously (3).

### 1. Dissolved Oxygen Depletion Rates

Two samples of stabilized sulfite-rich FGC wastes was tested for their effects on dissolved oxygen using a 2.5% slurry concentration with oxygen-saturated seawater under agitated conditions. The dissolved oxygen concentration in the slurry was monitored with time. A plot of these data is given in Figure 1. Additionally, data previously obtained for a sample of unstabilized direct lime FGD waste (L2) are shown for comparison. Since the total oxidizable sulfur (TOS) contents of the ST2 and ST3 wastes are much lower (1.34 and 2.99 mmoles per

TABLE 4

Major and Trace Chemical Composition of Waste Samples[a]

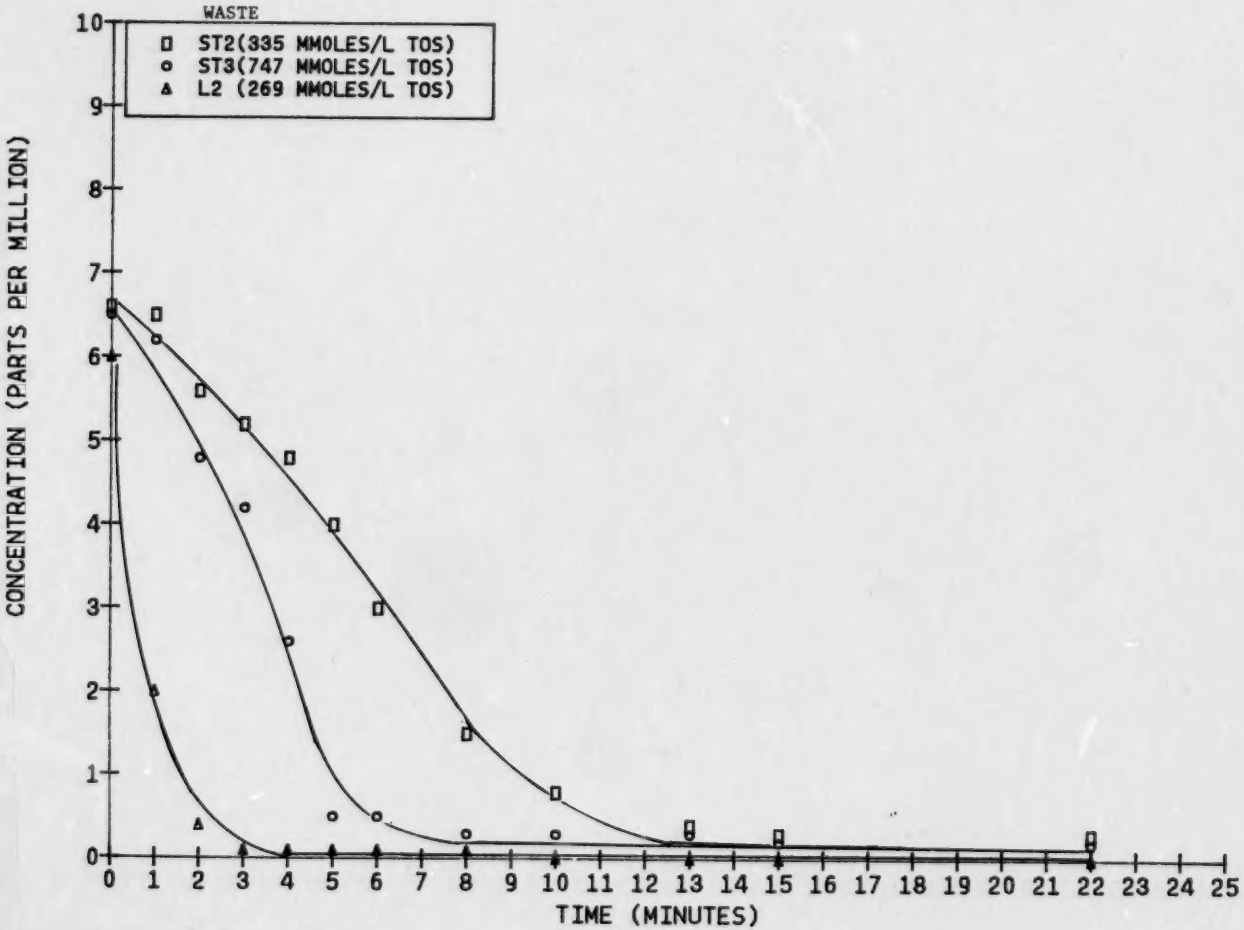
| Sample | Description | % Solids | Acid Insoluble (%) | Slurry pH | mm/g Ca | mm/g TOS | mm/g $SO_4$ | mm/g $CO_3$ | ppm[g] As | ppm[g] Cd | ppm[g] $Cr^{+6}$ | ppm[g] Cu | ppm[g] Ni | ppm[g] Se | ppm[g] Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Stabilized Samples** | | | | | | | | | | | | | | | |
| ST1 | Limestone (Sulfite-rich) | -- | -- | -- | -- | -- | -- | -- | 148 | 1.0 | 66 | 34 | 39 | 8 | 57 |
| ST2 | Limestone (Sulfite-rich) | 59 | 32 | 8.9 | 4.0 | 1.34 | 1.07 | 0.81 | 65 | 0.3 | 30 | 28 | 18 | 6 | 24 |
| ST3 | Limestone (Sulfite-rich) | 70 | 41 | 8.9 | 3.8 | 2.99 | 0.30 | 0.29 | 78 | 2.5 | 43 | 20 | 24 | 6 | 53 |
| ST4 | Forced Oxidation (Sulfate-rich)[b] | b | b | 10.2 | b | b | b | NA | 31 | 3.3 | 42 | 12 | 17 | 13 | 147 |
| **Unstabilized Samples** | | | | | | | | | | | | | | | |
| FO1 | Forced Oxidation (Sulfate-rich) | 80 | 41 | 8.9 | 4.6 | 0.02 | 3.38 | NA | 30 | 1.3 | 33 | 10 | 21 | 15 | 190 |
| FO2 | Flyash Scrubbing (Sulfate-rich) | 72 | 38 | 8.9 | 5.4 | 0.002 | 3.40 | NA | 83 | 0.6 | 47 | 40 | 23 | 11 | 147 |
| DA1 | Dual Alkali | 54 | 0 | NA | 7.15 | 5.52 | 0.97 | NA | NA | 0.29 | NA | NA | 11 | 15 | NA |
| L1 | Lime | 63 | 35 | NA | 4.59 | 3.85 | 0.70 | NA | NA | 0.8 | NA | NA | 44 | 19 | 59 |
| LS3 | Limestone | 79 | 38 | NA | 4.20 | 0.01 | 3.69 | NA | NA | 1.1 | NA | NA | 18 | 25 | 91 |

[a] Samples ST1, ST2, ST3, FO1, FOs and ST4 are from this work. Data for samples DA1, Li and LS3 are from part 1 of this report.
[b] Prepared from Sample FO1 by addition of 2% lime and 10% water.
[c] Dried at 85°C, 24 hours.
[d] In 1 Normal HCl.
[e] 20% slurry.
[f] NA=Not Analyzed.
[g] Data were taken from NEA Appendix to Part Two of this report.

Source: Arthur D. Little, Inc. and New England Aquarium.

FIGURE 1

DISSOLVED OXYGEN DEPLETION RATES




Source: Arthur D. Little, Inc.

gram, respectively) than that of the previously tested direct lime waste (5.76 mmoles/gram), the experiments with the stabilized wastes were performed at a much higher slurry concentration in order to compensate and make the results more directly comparable. Figure 1 provides the data for the TOS concentration present in the slurry at the start of each experiment.

As can be seen from Figure 1, depletion of the dissolved oxygen occurs for the three wastes at the tested slurry concentrations (2.5% suspended solids). As observed in previous tests, however, both the rate and amount depleted are dependent on the slurry concentration as well as the sulfite content of the waste (3). These data, however, do illustrate the following:

1. Stabilization of sulfite-rich FGD wastes does not tie up the sulfite sufficiently to prevent depletion of oxygen at the tested slurry concentrations.

2. The rate of depletion of oxygen is slower for the stabilized (relative to unstabilized) wastes under relatively similar conditions.

Support for the first observation also comes from the observed apparent solubility product for $CaSO_3$ in seawater obtained using the stabilized samples (see below). The second observation appears to be due to a slower release of soluble sulfite from the stabilized materials relative to the unstabilized samples (see below).

## 2. Calcium Sulfite Solubility and Rate of Dissolution

The relative rate of dissolution of $SO_3^{2-}$ from the stabilized, compared to unstabilized, wastes provides information on the extent to which sulfite is bound during the stabilization process. The product of the equilibrium calcium and sulfite concentrations provides information on the maximum concentration of sulfite expected in seawater (since it is expected to be limited by solubility of calcium sulfite). In addition,

if the observed solubility product is markedly different from that in unstabilized samples, it would provide evidence that a new sulfite species is formed in the stabilization process with a different solubility characteristic than calcium sulfite present in the unstabilized wastes.

The rate of sulfite dissolution was determined for the three sulfite-rich stabilized samples (ST1, ST2 and ST3). Sample ST1 was a brick-like material from the S.U.N.Y. program prepared as a block in the laboratory. It was ground prior to testing. Sample ST3 was mechanically broken up into smaller pieces prior to testing. Sample ST2 was not as cohesive as ST3 and crumbled into fine particles upon exposure to stirring in seawater. Several slurry concentrations (3-26%) were used to determine dissolution rates and the apparent solubility product.

The concentration of sulfite and calcium observed with time in the seawater in contact with the various wastes at various slurry concentrations are given in Table 5. The amount of Ca present at each sampling time in the seawater is also shown. Table 6 provides a summary of the best estimate for the solubility product determined for $CaSO_3$ from all of the samples. Figure 2 shows the rate of increase of sulfite in solution versus time for the stabilized samples. For comparison, data previously obtained (3) for unstabilized wastes are also shown.

As can be seen from Figure 2, the final sulfite concentration in the seawater ($3.7 - 4.7 \times 10^{-4}$ M) observed for the stabilized samples was much lower than for the unstabilized samples ($1.6 - 2.5 \times 10^{-3}$ M). The time required to reach 90% of the final concentrations was similar for both forms of the waste. Another difference is the total amount of calcium dissolved from the wastes into solution (Table 6). More calcium ions dissolved from the stabilized wastes relative to the sulfite suggesting that other species present in the waste also dissolved. This accounts for the lower sulfite present in solution. This is consistent with requiring dissolution of stabilization products

TABLE 5

Dissolution Data for Stabilized Sulfite-Rich Wastes
In Seawater

| Sample | Slurry Concentration (%) | Time(min) | $10^4 x[SO_3^{-2}]$,M | % of Final $[SO_3^{2-}]$ Value | $10^2[Ca^{2+}]$,M |
|---|---|---|---|---|---|
| ST1 | 20: | 60 | 4.3 | 100 | 3.6 |
| | | 120 | 3.5 | 81 | 3.5 |
| | | 180 | 4.4 | 102 | 3.6 |
| | | 1440 | 4.3 | 100 | 4.2 |
| ST2 | 20: | 60 | 1.3 | 28 | 3.4 |
| | | 120 | 1.6 | 35 | 3.5 |
| | | 180 | 1.5 | 33 | 3.5 |
| | | 300 | 1.8 | 39 | 3.5 |
| | | 360 | 4.6 | 100 | 4.3 |
| ST2 | 3: | 25 | 3.3 | 83 | 2.9 |
| | | 52 | 4.0 | 100 | 3.1 |
| | | 115 | 4.0 | 100 | 3.2 |
| ST2 | 8: | 31 | 2.7 | 73 | 2.6 |
| | | 58 | 3.6 | 97 | 3.1 |
| | | 125 | 3.7 | 100 | 3.4 |
| ST3 | 26: | 30 | 3.2 | 68 | 3.1 |
| | | 90 | 4.6 | 98 | 3.2 |
| | | 120 | 4.4 | 94 | 3.2 |
| | | 1440 | 4.7 | 100 | 4.2 |
| ST3 | 8: | 25 | 3.9 | 75 | 1.9 |
| | | 48 | 4.9 | 94 | 1.9 |
| | | 112 | 5.2 | 100 | 2.1 |

Source: Arthur D. Little, Inc.

TABLE 6

Apparent Solubility Product for Calcium Sulfite in Seawater[d]

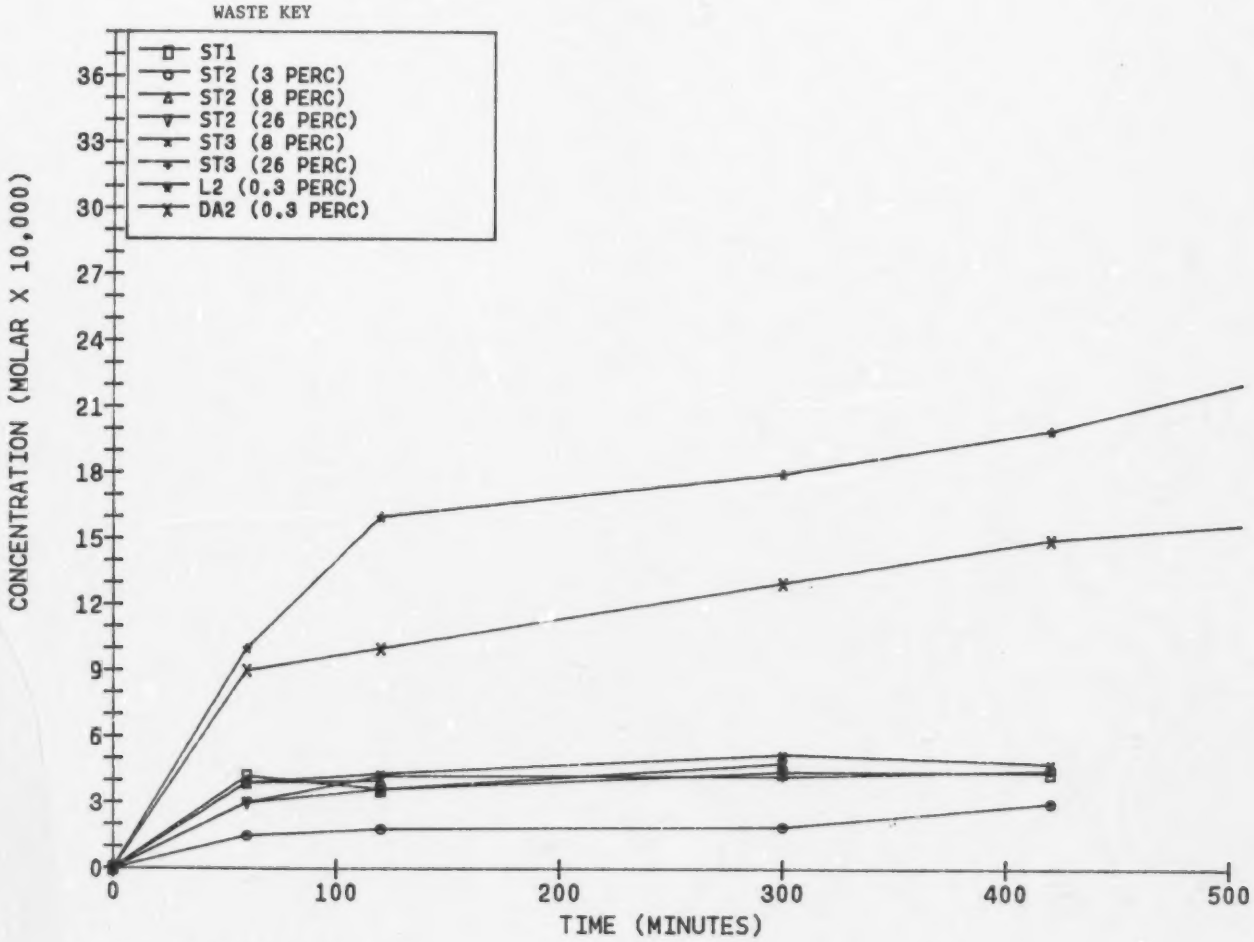
| Sample | % Slurry | Contact Time | $[SO_3^{2-}]$,M | $[Ca^{2+}]$Total,M | $[Ca^{2+}x[SO_3^{2-}]$ |
|---|---|---|---|---|---|
| **Stabilized Wastes** | | | | | |
| ST1 [a] | 20 | 1440 | $4.3x10^{-4}$ | $4.2x10^{-2}$ | $1.8x10^{-5}$ |
| ST2 [b] | 20 | 360 | $4.7x10^{-4}$ | $4.3x10^{-2}$ | $2.0x10^{-5}$ |
| ST2 [b] | 8 | 125 | $3.7x10^{-4}$ | $3.4x10^{-2}$ | $1.3x10^{-5}$ |
| ST2 [b] | 3 | 115 | $4.0x10^{-4}$ | $3.2x10^{-2}$ | $1.3x10^{-5}$ |
| ST3 [a] | 26 | 1440 | $4.3x10^{-4}$ | $4.2x10^{-2}$ | $1.4x10^{-5}$ |
| ST3 [a] | 8 | 112 | $5.2x10^{-4}$ | $2.1x10^{-2}$ | $1.1x10^{-5}$ |
| | | | | Range: | $(1.1\text{-}x2.0)x10^{-5}$ |
| **Unstabilized Wastes**[c] | | | | | |
| DA2 | 0.3 | 180 | $1.6x10^{-3}$ | $1.4x10^{-2}$ | $2.2x10^{-5}$ |
| DA3 | 1.3 | >30 | $1.9x10^{-3}$ | $1.7x10^{-2}$ | $3.2x10^{-5}$ |
| L1 | 1.2 | >30 | $2.3x10^{-3}$ | $1.2x10^{-2}$ | $2.7x10^{-5}$ |
| L2 | 1.0 | 30 | $2.3x10^{-3}$ | $1.4x10^{-2}$ | $3.2x10^{-5}$ |
| L2 | 0.3 | 210 | $2.3x10^{-3}$ | $1.2x10^{-2}$ | $2.8x10^{-5}$ |
| | | | | Range: | $2.2\text{-}3.2x10^{-5}$ |

[a] Samples were groundup prior to slurry formation
[b] Samples dispersed upon contact with seawater
[c] Data from Ref 3.
TOS Concentration in these wastes were: DA2 5.49 mm/g, L2 5.76 mm/g, Li 3.84 mm/g, DA3 2.69 mm/g
[d] Data are for room temperatures

Source: Arthur D. Little, Inc.

FIGURE 2

## SULFITE DISSOLUTION RATES




Source: Arthur D. Little, Inc.

prior to availability of the sulfite. The solubility product obtained using the stabilized samples is very similar to the value determined previously (see Table 6). The difference between the two values is possibly experimental error. The lower concentration of dissolved sulfite at a given contact time in the stabilized sample slurries is consistent with the lower rate of depletion of dissolved oxygen previously noted.

It is apparent that availability of sulfite is reduced in the stabilized samples even though they were ground and higher percent slurries of them were used (relative to the unstabilized samples).

## D. Quiescent Leaching Tests

### 1. Experimental Design

This test was designed to measure the extent of migration of trace components from the waste into the seawater under conditions where the waste is not actively agitated with the seawater. The experimental design and apparatus and other associated procedures are discussed in Part One of this report and details are provided in the Part One and Part Two Appendices. In Part Two, five waste samples were tested (FO1, FO2, ST2, ST3 and ST4). Along with the five leaching tanks, two other tanks were monitored. The first was a background tank and the other a spiked seawater tank (to check on stability of trace element in the tanks during the test period). The bulk surface area of the waste samples exposed to the seawater in the test tanks was 1267 $cm^2$. Thirteen liters of seawater (10 cm height) was placed above the wastes. The waste heights were about 3 cm. Leaching was carried out for 28 days. Water above the waste was stirred slowly to maintain homogeneity but not sufficient to suspend any waste material. Aliquots (500 ml, except when duplicate analyses were performed) were taken at different time period during the test. Chemical analyses of the seawater in each tank were performed for pH, As, Cr, Cu, Cd, Zn, Ni, Se, and Hg.

## 2. Results and Discussion

Since the concentrations of the trace elements observed in this test in the seawater phase are a function of the particular test design (specifically seawater volume to waste surface area ratio), it is useful to express the results of these tests in terms of total amount of trace element leached per sampling time per fixed amount of surface area. This facilitates comparison with the results of the previous tests. The total quantity leached should be independent of seawater volume if mechanisms within the waste are governing release and the trace elements of interest are not exhibiting solubility limitations in the seawater.

Tables 7 through 11 provide the cumulative amount of the elements released present in the seawater phase at various sampling times (including any previous amount removed by prior samples) for the various stabilized waste samples. These data are uncorrected for background seawater and are for 1267 $cm^2$ of waste surface area. The trace elements have been assumed not to be solubility limited in any case. Table 12 and 13 provide the data in similar form for the background tank and the stability test tank.

Plots of the total amount released versus time for selected samples for Cd, Se, As, and Cr are provided, respectively, in Figures 3, 4, 5 and 6.

A comparison of the total amount leached after the end of the test for both stabilized and unstabilized wastes after correction for the seawater background is given in Table 14.

TABLE 7

Cumulative Amount of Trace Metals Released per Time
For Forced Oxidation and Stabilized Wastes* in Micrograms

Data for FO1

| Time (days) | Cd | Zn | Ni | Se | As | Cr | Cu |
|---|---|---|---|---|---|---|---|
| 1 | 9 | 161 | 43 | <78 | <130 | 130 | 5 |
| 2 | 15 | 176 | 29 | 72 | 205 | 243 | 5 |
| 4 | 35 | 195 | 40 | 121 | 289 | 362 | 20 |
| 7 | 51 | 169 | 34 | 121 | 277 | 480 | 4 |
| 14 | 83 | 280 | 31 | 142 | 361 | 491 | <5 |
| 21 | 93 | 191 | 39 | 192 | 422 | 121 | <4 |
| 28 | 101 | 148 | 36 | 268 | 384 | 545 | <4 |

*Uncorrected for control tank concentrations, total surface area of waste in the quiescent leaching test was 1267 $cm^2$.

Source: New England Aquarium and Arthur D. Little, Inc.

TABLE 8

Cumulative Amount of Trace Metals Released Per Time
For Forced Oxidation and Stabilized Wastes* in Micrograms

Data for FO2

| Time (days) | Cd | Zn | Ni | Se | As | Cr | Cu |
|---|---|---|---|---|---|---|---|
| 1 | <7 | 95 | 94 | 91 | <130 | 377 | 10 |
| 2 | <4 | 112 | 136 | 216 | <130 | 703 | 19 |
| 4 | <5 | 15 | 140 | 72 | <130 | 810 | 17 |
| 7 | <6 | 39 | 79 | 185 | <130 | 891 | 19 |
| 14 | 12 | 48 | 54 | <90 | <130 | 990 | 28 |
| 21 | 19 | 87 | 68 | 307 | <130 | 1326 | 22 |
| 28 | <10 | 97 | 80 | 345 | <130 | 1296 | 16 |

*Uncorrected for control tank concentrations, total surface area of waste in the quiescent leach test was 1267 $cm^2$

Source: New England Aquarium and Arthur D. Little, Inc.

TABLE 9

Cumulative Amount of Trace Metals Released per Time
For Forced Oxidation and Stabilized Wastes* in Micrograms

Data for ST2

| Time (days) | Cd | Zn | Ni | Se | As | Cr | Cu |
|---|---|---|---|---|---|---|---|
| 1 | <8 | <5 | 33 | 247 | <130 | <26 | 4 |
| 2 | <5 | 75 | 25 | 79 | <130 | <26 | 7 |
| 4 | 7 | <6 | 15 | 91 | <130 | <48 | 5 |
| 7 | <3 | 8 | 13 | 124 | <158 | <27 | <2 |
| 14 | 13 | 18 | 12 | 125 | <170 | <16 | <5 |
| 21 | <6 | 44 | 15 | 145 | <160 | <27 | <4 |
| 28 | 33 | 38 | 20 | 117 | <124 | <26 | <4 |

*Uncorrected for control tank concentrations, total surface area of waste in the quiescent leaching test was 1267 $cm^2$.

Source: New England Aquarium and Arthur D. Little, Inc.

TABLE 10

Cumulative Amount of Trace Metals Released per Time
For Forced Oxidation and Stabilized Wastes* in Micrograms

Data for ST3

| Time (days) | Cd | Zn | Ni | Se | As | Cr | Cu |
|---|---|---|---|---|---|---|---|
| 1 | <12 | 55 | 17 | <104 | <130 | 39 | 9 |
| 2 | <4 | 51 | 27 | 50 | <130 | <25 | 14 |
| 4 | <4 | 18 | 25 | 74 | <130 | 74 | 17 |
| 7 | <6 | 13 | 23 | 75 | 201 | <23 | 13 |
| 14 | <4 | <9 | 42 | 170 | 271 | <22 | 14 |
| 21 | 11 | 63 | 26 | 220 | 365 | 53 | 12 |
| 28 | <8 | 111 | 29 | 230 | 403 | 40 | 13 |

*Uncorrected for control tank concentrations, total surface area of waste in the quiescent leaching test was 1267 $cm^2$

Source: New England Aquarium and Arthur D. Little, Inc.

TABLE 11

Cumulative Amount of Trace Metals Released per Time
For Forced Oxidation and Stabilized Wastes* in Micrograms

Data for ST4

| Time (days) | Cd | Zn | Ni | Se | As | Cr | Cu |
|---|---|---|---|---|---|---|---|
| 1 | <9 | 113 | 16 | <101 | <130 | 79 | 7 |
| 2 | <5 | 88 | 26 | 113 | <130 | 42 | 14 |
| 4 | <7 | 45 | 12 | 208 | <130 | 209 | <3 |
| 7 | <6 | 38 | 15 | 204 | <130 | 232 | <5 |
| 14 | 35 | 74 | 23 | 97 | <130 | 363 | <5 |
| 21 | 13 | 147 | 12 | 244 | <160 | 425 | <5 |
| 28 | 21 | 51 | 14 | 196 | <150 | 478 | <4 |

*Uncorrected for control tank concentrations, total surface area of waste in the quiescent leaching test was 1267 $cm^2$.

Source: New England Aquarium and Arthur D. Little, Inc.

TABLE 12

TOTAL AMOUNT OF TRACE ELEMENTS PRESENT IN BACKGROUND TANK[a]

| Time (days) | Cd | Zn | Ni | Se | As | Cr | Cu |
|---|---|---|---|---|---|---|---|
| 1 | <10 | 82 | 40 | <104 | <130 | <13 | 10 |
| 2 | <4 | 116 | 31 | <42 | <130 | <25 | 18 |
| 4 | <5 | 140 | 38 | <64 | <130 | 16 | 8 |
| 7 | <2 | 144 | 36 | 92 | <130 | <14 | 17 |
| 14 | 14 | 164 | 37 | <78 | <130 | <8 | 18 |
| 21 | <6 | 105 | 33 | <89 | <130 | 42 | 15 |
| 28 | <7 | 97 | 33 | <78 | <130 | 20 | 16 |

[a]All data in µg.

Source: New England Aquarium and Arthur D. Little, Inc.

TABLE 13

Stability of Trace Elements in Seawater Tank[a,b,c,]

Stability Study in Seawater

| Time (days) | Cd | Zn | Ni | Se | As | Cr(VI) | Cu | Hg |
|---|---|---|---|---|---|---|---|---|
| 1 | 287 | 386 | 270 | 247 | 273 | 52 | 181 | 280 |
| 2 | 250 | 327 | 256 | 273 | 135 | 40 | 162 | 175 |
| 4 | 245 | 327 | 248 | 248 | 267 | 40 | 151 | 106 |
| 7 | 261 | 333 | 271 | 226 | 207 | <17 | 162 | 51 |
| 14 | 269 | 323 | 241 | 278 | 165 | 40 | 160 | 51 |
| 21 | 270 | 331 | 268 | 258 | 264 | 40 | 149 | <48 |
| 28 | 320 | 288 | 308 | 201 | 176 | 50 | 171 | <46 |

[a]Metals added to seawater in the following forms: Cd(II), Zn (II), Ni (II), Se (IV), As (III), Cr (VI), Cu (II), Hg (II). All data in µg.

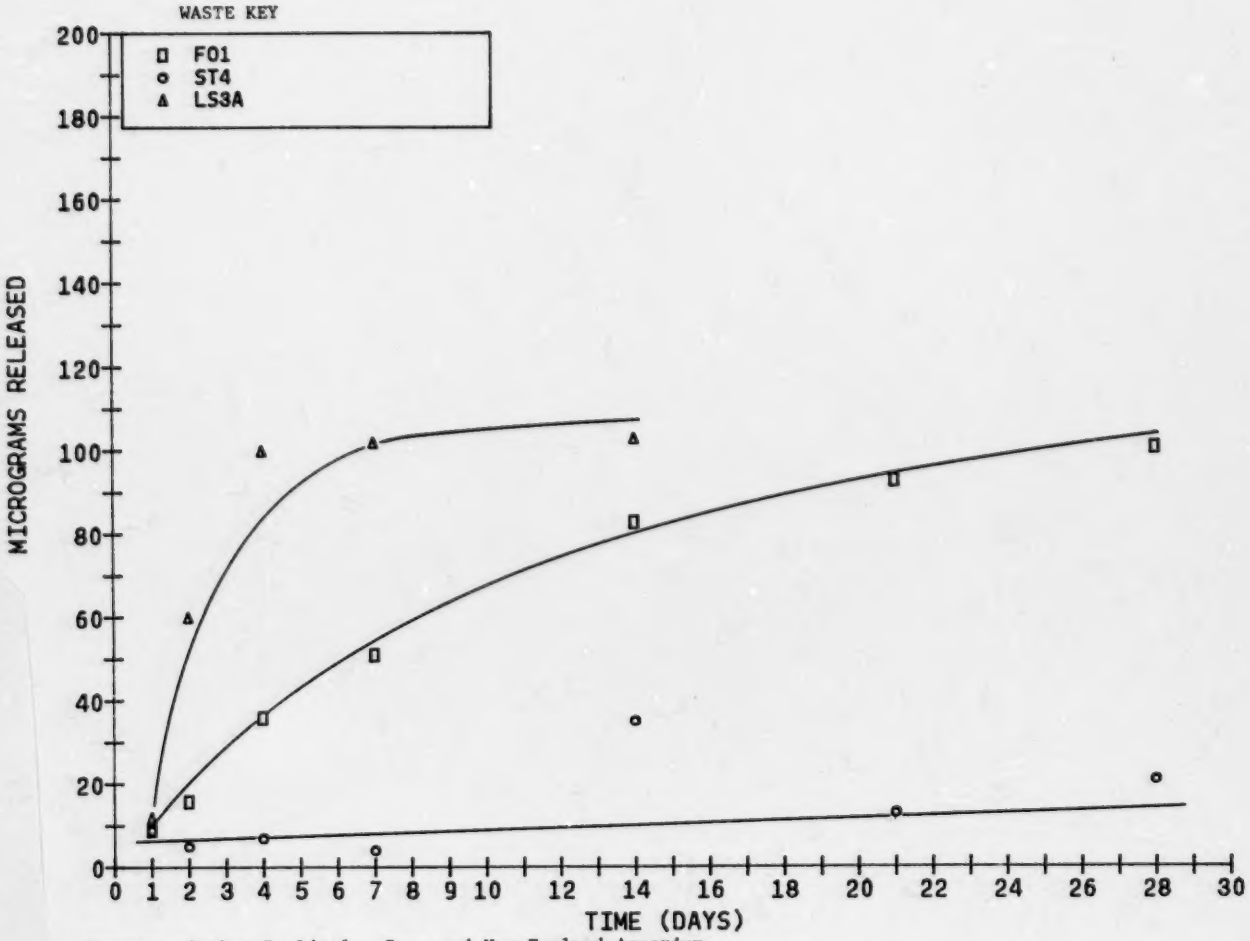
[b]Cr (III) stability was poor (loss from 20 ppb to 4 ppb in 6 hours).

[c]No stabilization attempted. Data expressed on same basis as sampling protocol used for data for stabilized samples.

Source: New England Aquarium and Arthur D. Little, Inc.

FIGURE 3

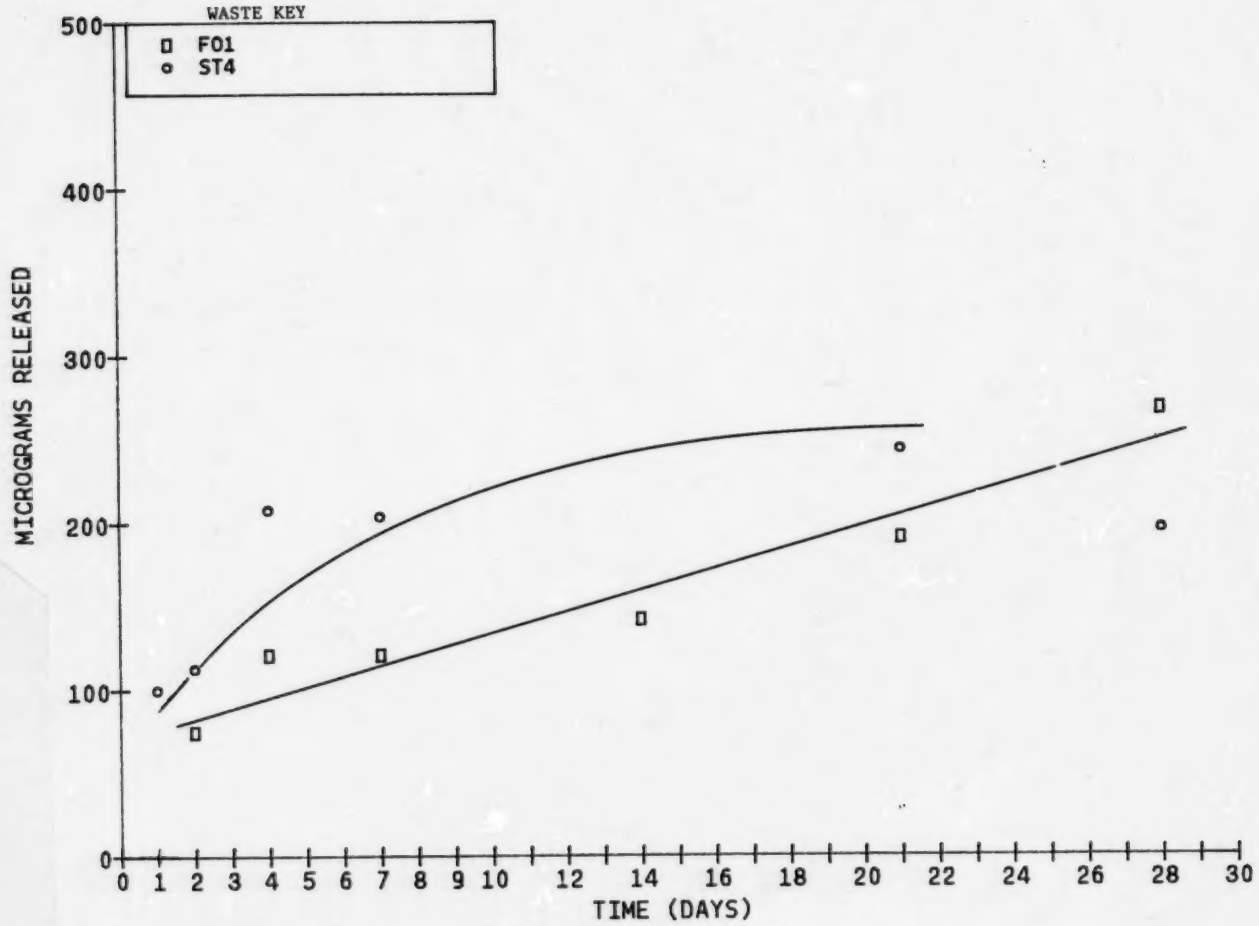
## CADMIUM RELEASE




Source: Arthur D. Little, Inc. and New England Aquarium

FIGURE 4

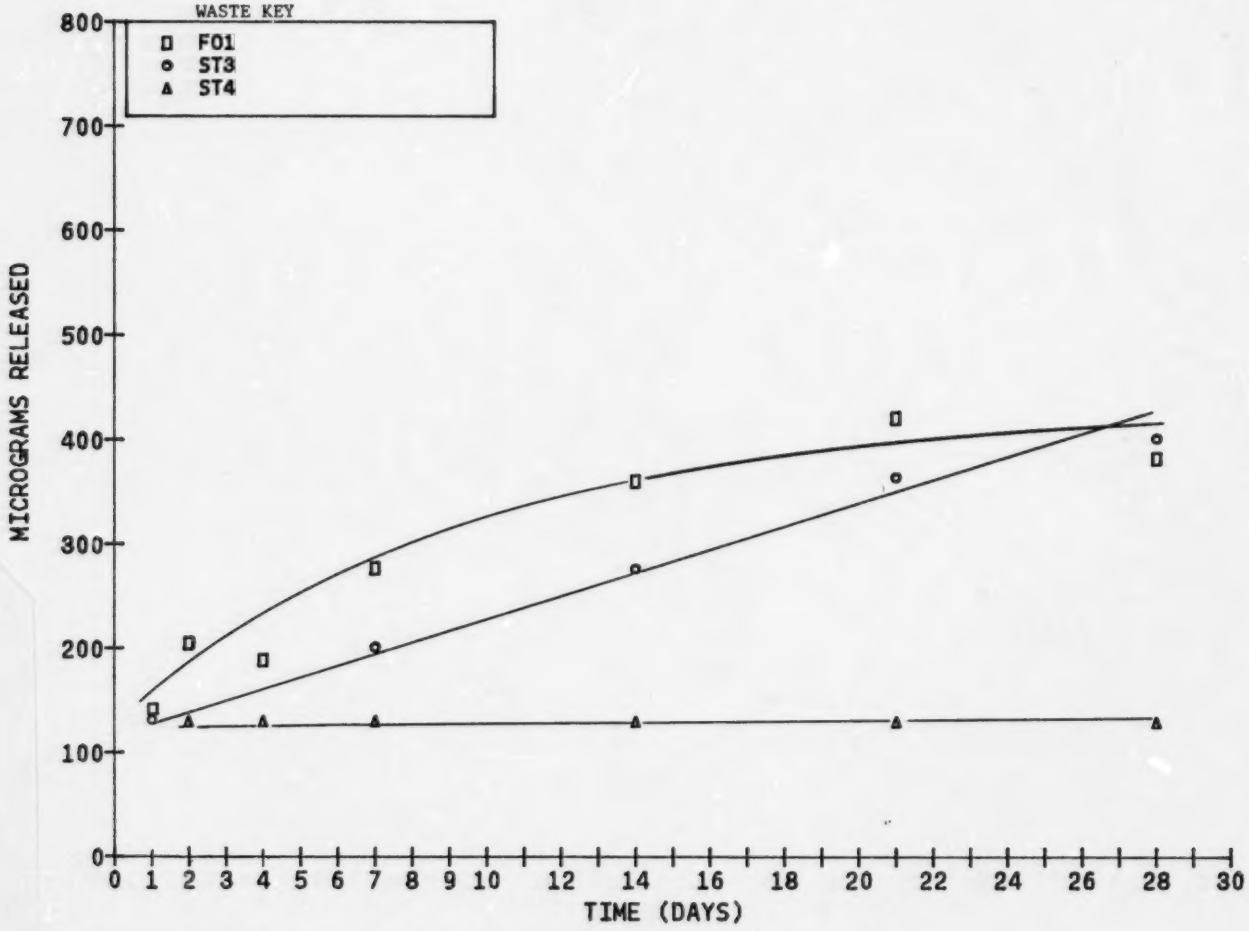
SELENIUM RELEASE




Source: Arthur D. Little, Inc. and New England Aquarium

FIGURE 5

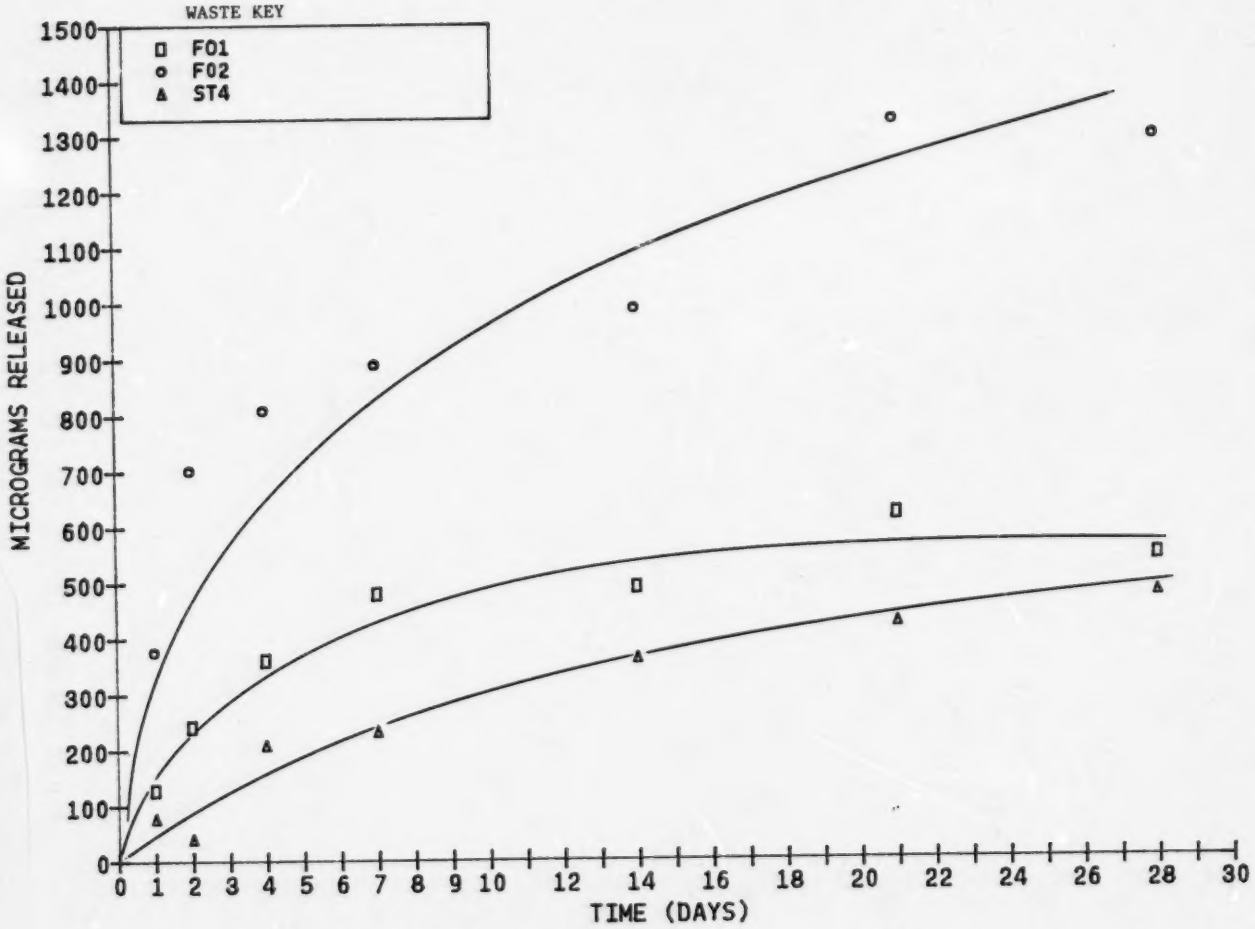
ARSENIC RELEASE




Source: Arthur D. Little, Inc. and New England Aquarium

FIGURE 6

CHROMIUM RELEASE




Source: Arthur D. Little, Inc. and New England Aquarium

TABLE 14

Cumulative Amount of Trace Elements Leached Into Seawater (Per 1000 $cm^2$ Surface Area After 4 Weeks)[k]

| Sample[a] | Notes[i] | Cd(µg) | Zn(µg) | Ni(µg) | Se(µg) | As(µg) | Cr(µg) | Cu(µg) | pH |
|---|---|---|---|---|---|---|---|---|---|
| DA1 | j,e | BDL[g] | BDL | BDL | BDL | -- | -- | -- | -- |
| L1 | j,e | 21 | BDL | 154 | 809 | -- | -- | -- | -- |
| LS3(1) | j,e | 126 | BDL | BDL | 388 | -- | -- | -- | -- |
| LS3(2) | j,e | 149 | BDL | BDL | 637 | -- | -- | -- | -- |
| LS3(3) | j,e | 212 | BDL | BDL | 679 | -- | -- | -- | -- |
| FO1*** | i,b,f,d | 79 | 57 | 8 | 211 | 303 | 417 | -13 | 8.0 |
| FO2 | i,b,f,d | <10 | -17[c] | 43 | 272 | <102 | 1010 | 3 | 8.5 |
| ST2 | i,b,f,d | 26 | -30 | -5 | 92 | <102 | <20 | -10 | 8.2 |
| ST3 | i,b,f,d | <7 | +28 | -2 | 182 | 318 | 19 | 0 | 8.1 |
| ST4 | i,b,f,d | 17 | -20 | -10 | 155 | <102 | 365 | -10 | 8.3 |
| Control Tank[d] (Contents of seawater background) | | <7 | 76 | 26 | <61 | <102 | 16 | 13 | 8.1 |

[a]DA = Dual Alkali  L = Lime  LS = Limestone  FO = Forced Oxidation  ST = Stabilized (lime/fly ash)

[b]Corrected for background concentration of seawater.

[c]Negative Value Indicates Loss from Solution.

[d]Data for this work after 28 days.

[e]Data for Part One tests after 31 days.

[f]Less than value treated as zero for calculations purposes.

[g]BDL = Below Detection Limit.

[h]Seawater solutions.

[i]This work surface area originally 1267 $cm^2$.

[j]Derived from previous NEA study. Surface area originally was 2125 $cm^2$.

[k]Data for Hg not included since a spiked control showed loss of Hg from the tanks after 7 days.

Source: New England Aquarium and Arthur D. Little, Inc.

Arsenic

Arsenic was released (approximately 300% above background) for samples FO1 and ST3 (which had, respectively, levels of 30 and 78 ppm As in the solid). No release was observed for FO2, ST2 and ST4, which had As in the range of 31 to 83 ppm in the solid. A reduction in the quantity leached was observed upon stabilization of the FO1 forced oxidation sample (subsequently ST4). As seen from Figure 5, sample FO1 exhibits a different pattern of release than sample ST3. Release from sample FO1 appears to slow down after 28 days while that for ST3 is still continuing.

Selenium

The selenium data suggest that stabilization does not have a great effect on changing the rate of release of this element. Comparison of the data for FO1 to ST4 suggests similar quantities released although the stabilized sample shows a different pattern (Figure 4). In addition, although all the forced oxidation samples show lower levels of Se released per 1000 $cm^2$ area than the unstabilized samples it should be noted that they also contained less selenium in the solid (6-15 ppm) than the unstabilized samples (19 and 25 ppm).

Copper

Copper showed similar behavior for all samples, showing essentially no release from the samples. In some cases reductions of up to 100% of the total amount present in background were observed. Losses from the seawater are consistent with adsorption on the waste surfaces. No change was evident upon stabilization of sample FO1.

Cadmium

The cadmium data showed release of Cd for FO1 and smaller releases for ST2 and ST4. Sample FO1 with a Cd value of 1.3 ppm indicated a release of greater than 79 ug (greater than 1100% of background).

Stabilization of the FO1 sample produced a reduction in quantity released. In general, the stabilized samples (with greater Cd level in the solids) released less Cd than their unstabilized counterparts (which contained relatively lesser amounts of Cd in the solids). In this instance stabilization apparently reduced the Cd released. A plot of the amount released with time (Figure 3) for FO1, ST4 and LS3 (A) waste samples shows that the pattern of release is different for these samples, and suggests greater availability (rate) of release for LS3 than FO1 and ST4.

Zinc

The data for Zn release for the stabilized and additional forced oxidation wastes are very similar to that obtained in the earlier tests for the unstabilized wastes (see Part One). A decrease of Zn from the seawater solution was observed for many of the samples, suggesting adsorption (6-42% of the original Zn present in seawater) of the ion onto the waste for three of the five new samples studied. The Zn content of these three wastes was similar to that of the previously tested unstabilized samples (24-147 ppm). For two samples of wastes (FO1 and ST3) with a Zn content of 190 and 53 ppm, respectively, small releases of Zn above background were noted (37-74%). The difference between FO1 and ST4 suggests that stabilization did reduce the amount of zinc released.

Nickel

The data for nickel release were similar to those for Zn in that adsorption of Ni from seawater onto the waste (10-38% of the Ni in seawater) apparently occured during the 28 days for the stabilized waste samples. These samples had Ni in the range of 17-24 ppm. The FO2 sample, with nickel content of 23 ppm, had a release of nickel of 165% above background. In general, a difference between unstabilized and stabilized samples was observed. Comparison of FO1 and ST4 (stabilized and unstabilized samples of the same forced oxidation waste) also supports this observation.

## Chromium

Chromium release was variable depending on the samples. Concentration of chromium in the solids ranged between 30 and 66 ppm. Stabilization of sample FO1 did not produce a great reduction in total amount released (a change of 12%) after 28 days. The shapes of the release *versus* time curves are also very similar (Figure 6) for these samples. The other stabilized samples (ST2 and ST3) with chromium concentrations of 30 and 43 ppm in the solids, respectively, did not release any detectable chromium. The unstabilized forced oxidation samples, FO1 and FO2 (which had chromium concentrations of 33 and 47 ppm, respectively in the solid), showed great amounts of release at amounts of 2600% to 6300% that are present in the background tank. Of particular significance in the chromium data is the additional fact that chromium was speciated as to the fraction present as Cr (VI) *versus* total chromium. Chromium (VI) was measured by APDC extraction of the seawater followed by plasma emission. Total chromium was measured directly in the seawater by plasma emission. The chromium leached into the seawater (range of 100-121%) was found to be all present in the Cr (VI) form for extracts of samples FO1, FO2 and ST4 which had measurable chromium levels (see Appendix). As also noted in the Appendix, the stability of Cr (III) in the seawater tanks was very poor (loss of 20 ppb to 4 ppb in 6 hours) and thus any chromium (III) leached from the wastes could have been lost due to adsorption on the container, leaving only Cr (VI) to be measured in solution.

## Mercury

Attempts to quantitate Hg in these leachates, in general, showed less than detection levels for most of the samples. This is consistent with the observation that Hg was not stable in the seawater control tanks during the test period and does not necessarily imply that Hg is not released from the wastes.

## Summary Comparison of Unstabilized Sulfate-Rich Samples

Table 15 presents an overall comparison of the leaching test results for the common analytes in the relatively toxic LS-3 waste tested previously and the two other unstabilized, forced-oxidation wastes tested in this part. Discussion of the way in which these results were translated into exposure conditions for the bioassay tests appears in Section IV.A. below.

Table 15

Trace Elements Leached from Sulfate-Rich,
Unstabilized FGD Wastes into Seawater:
A Comparison of Results from 1978 and 1982

| | | | Concentration (ug/L) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | SA/Vol | | Cd | | Ni | | Se | | Zn | |
| 1978 | | Day | 14 | 31 | 14 | 31 | 14 | 31 | 14 | 31 |
| LS3 waste | 1:7.5 | | 9 | 26 | 8 | 28 | 56 | 64 | 16 | 35 |
| | 1:15 | | 7 | 18 | 10 | 18 | 26 | 54 | 18 | 12 |
| | 1:23 | | 6 | 9 | 7 | 10 | 19 | 33 | 14 | 14 |
| 1982 | | Day | 14 | 28 | 14 | 28 | 14 | 28 | 14 | 28 |
| FO1 waste | 1:10 | | 7 | 9 | 3 | 11 | 12 | 25 | 23 | 11 |
| FO2 waste | 1:10 | | 1 | <1 | 3 | 6 | <6 | 32 | 1 | 9 |

Source: New England Aquarium

## IV. BIOLOGICAL TESTING

### A. Experimental Design

The bioassay tests conducted as part of this effort were designed to parallel as closely as possible the series of thirty-day exposure tests conducted earlier in the program and described in detail in Part One of this report. Details of the experimental design for Part Two are presented in the Appendix prepared by the NEA investigators, and include description of the equipment and procedures employed. The following discussion briefly summarizes the waste and organism types used in the Part Two tests, and the rationale for selection of trace element levels maintained in the tests.

#### Wastes

Wastes used in addition to a control tank for this series of exposure tests were as follows:

FO1 - an unstabilized, forced-oxidation FGC waste from the same plant/system as produced the LS-3 waste that proved highly toxic in the Part One tests;

FO2 - a trace metal-rich, unstabilized forced-oxidation FGC waste produced at full-scale;

ST2 - a sulfite-rich, soil-like stabilized FGC waste produced by the CSI process at full-scale;

ST3 - similar to ST2, but yielding higher concentrations of leached trace metals in seawater; and

ST4 - a stabilized version of FO1 produced at laboratory scale.

## Test Species

Two of the test species used in the Part One tests were used again in this series of tests: the soft-shell clam (Mya arenaria) and the snail (Littorina littorea). A third species, the polychaete worm Nereis virens, was added to the experiment in place of other species (flounder and eel grass) that proved relatively poor indicators in the previous tests.

## Trace Element Levels Used in the Exposure Tests

As in the previous experiments using unstabilized wastes, the trace element concentrations to which the organisms were exposed were determined from the results of the quiescent leaching tests. It was assumed that most of the exposed organisms would reside at the bottom of the tanks and thus would be exposed to the trace element levels characteristic of that part of the water column. Thus, a reasonable "conservative" condition was to assume levels as would be obtained if the trace element leached in the quiescent tests at 28 days into a layer of relatively quiescent seawater 8 cm in height above the waste. These conditions were similar to those in the unstabilized waste tests reported in Part One (31 day leach data into 8 cm of seawater).

The trace elements were added using concentrated stock solutions prepared from the following compounds in nitric acid acidified solutions. Selenium was added as $H_2SeO_3$ [Se (IV)], arsenic as $As_2O_3$ [As (III)], chromium as $K_2CrO_4$ [Cr (VI)] and cadmium as $CdCl_2$ [Cd (II)].

Addition of these elements in their respective oxidation states was considered reasonable for the following reasons. Selenium is likely to exist as either Se°, Se (IV) or Se (VI) and since Se° is not very soluble and Se (VI) is a good oxident (oxidizing $Cl^-$) it is likely that having been leached from the waste the selenium will end up as Se (IV). Cadmium would occur under these conditions as cadmium (II) complexed with hydroxide and/or chloride. Chromium was added as Cr (VI) based on

experimental measurement of total dissolved chromium (by analysis of extracts of day 21 and day 28 samples of FO1, FO2 and ST4 directly using DC plasma emission) and Cr (VI) in these extract samples (by APDC extraction followed by DC plasma analysis). These results suggest that all of the chromium present in the extracts from these wastes (FO1, FO2 and ST4) was in the chromium VI oxidation state.

The concentrations of trace elements used in the long term exposure tests is given in Table 16, along with a comparison of these levels to the concentrations observed in the quiescent leaching tests after 28 day leaching of the waste.

## B. Results and Discussion

### 1. Acute and Chronic Toxicity

As illustrated in Table 17, the incidence of organism mortalities in the Part Two test series was minimal. In particular, it is noteworthy that mortalities among the clams (Mya) and snails (Littorina) that proved extremely sensitive to the water in the LS-3 waste tank in 1978 were negligible to insignificant in the FO1 and FO2 waste tanks in 1982. In fact, no clams died in either of these tanks in 1982, while all the clams died before the end of the previous comparable test in the LS-3 tank (see Part One of this report). These data tend to confirm the hypothesis that the incidence of mortality observed in the Part One test was a relatively unique phenomenon.

For the two trace metals new to this series of tests (As and Cr), the water column concentrations sustained in the test tanks (see Table 16) were generally below reported acute toxicity thresholds for representative marine organisms. Specifically, the As levels were below the Final Acute Value of 67 ug/l established by the EPA (4) and the $Cr^{+6}$ levels were, with one exception, below the zero mortality levels reported by Eisler and Hennekey for six common marine/estuarine species (5). Selenium levels were below the EPA's Final Invertebrate

TABLE 16

Trace Element Concentrations (ppb) in Seawater for Quiescent Leaching Tests and for Long-Term Bioassay Tests

| Element | | FO1 | FO2 | ST2 | ST3 | ST4 | Boston Harbor[b] Seawater |
|---|---|---|---|---|---|---|---|
| As | Leaching Test[a] | 33 | <10 | <10 | 38 | 15 | <10 |
| | Bioassay[d] | 62 | 15 | 12 | 54 | 22 | |
| Cd | Leaching Test | 9.3 | 1 | 4 | 2 | 3 | <0.2-1.3 |
| | Bioassay | 16 | 1 | 4 | 2 | 3 | |
| Cr | Leaching Test | 47 | 109 | <2 | 4 | 42 | <0.4-4 |
| | Bioassay | 75 | 135 | <6 | <6 | 52 | |
| Se | Leaching Test | 25 | 32 | 8 | 21 | 16 | <6 |
| | Bioassay | 36 | 39 | 11 | 16 | 15 | |
| Cu[c] | Leaching Test | <0.2 | 1.1 | <0.2 | 1.1 | <0.2 | 0.7-1.5 |
| Ni[c] | Leaching Test | 3 | 6 | 1.5 | 2.3 | 1.1 | 2.4-3.1 |
| Zn[c] | Leaching Test | 10 | 8.6 | 3.4 | 11 | 3.1 | 6.3-13.4 |

[a] Data for 28 day leaching period actual concentration in tanks.
[b] Data taken from control tank.
[c] These elements were not spiked into seawater during the long term toxicity tests.
[d] Data reported as the actual levels measured (see Appendix).

Table 17

Mortalities Occuring

During the Bioconcentration Study

| Day | Tank | FGDS | Mya | Nereis | Littorina | "tails" |
|---|---|---|---|---|---|---|
| 5 | 4 | FO2 | - | - | - | 2 |
| 6 | 2 | FO1 | - | - | - | 1 |
| | 4 | FO2 | - | - | - | 1 |
| | 6 | CTRL | - | - | - | 2 |
| 9 | 2 | FO1 | - | 1 | - | 1 |
| | 4 | FO2 | - | - | - | 1 |
| 11 | 4 | FO2 | - | 1 | - | - |
| 12 | 1 | ST3 | 1 | - | - | - |
| 13 | 3 | ST4 | 1 | - | - | - |
| 19 | 2 | FO1 | - | - | 1 | - |
| 23 | 1 | ST3 | 1 | - | - | - |
| 35 | 4 | FO2 | - | - | 2 | - |
| | 5 | ST2 | 1 | - | - | - |
| 37 | 3 | ST2 | 1 | - | - | - |
| 40 | 6 | CTRL | 1 | - | - | - |
| Total | | | 6 | 2 | 3 | 8 |

By Material:

| | Treatment | | | | | |
|---|---|---|---|---|---|---|
| | CTRL | FO1 | FO2 | ST2 | ST3 | ST4 |
| Mya | 1 | - | - | 2 | 2 | 1 |
| Littorina | - | 1 | 2 | - | - | - |
| Nereis | - | 1 | 1 | - | - | - |
| "tails" | 2 | 2 | 4 | - | - | - |

Source: New England Aquarium

Saltwater Chronic Value of 47 ug/l (4). Cadmium levels were at or below the EPA's Final Saltwater Acute Value of 16 ug/l (4).

The snails characteristically preferred the glass tank walls to other substrates in all of the test tanks, including the control. None of the other test organisms exhibited avoidance behavior with respect to the FGC waste substrates. In fact, in at least one instance the marine worms appeared to prefer the wastes to the available alternative of more coarse sand that covered half of the tank bottom (see Appendix).

## 2. Bioaccumulation

### Arsenic

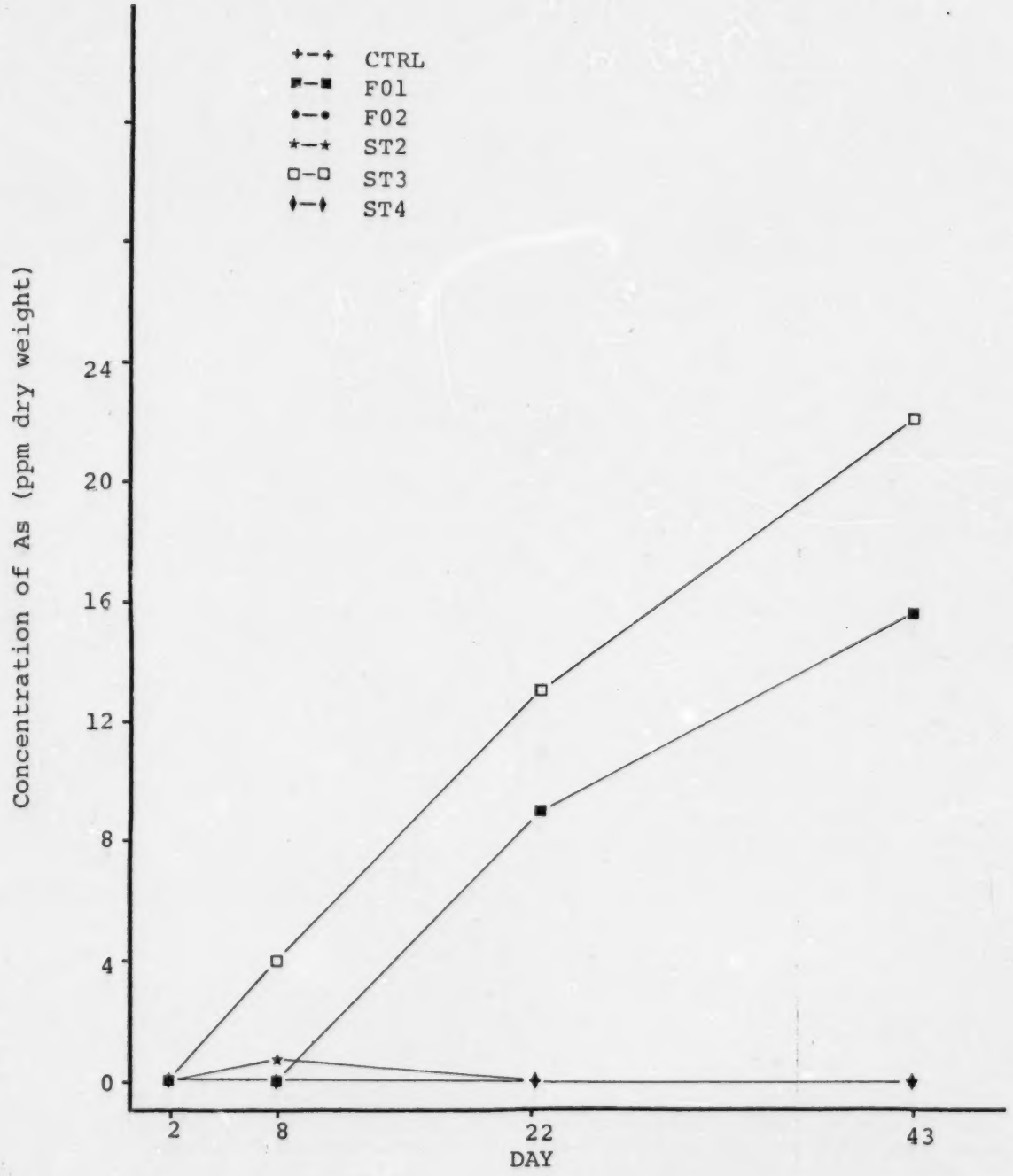
Figures 7 and 8 (a-b) illustrate the test results for bioaccumulation of As. Note that only in the snails in the FO1 and ST3 waste tanks was there appreciable, and increasing arsenic accumulation. In Figure 9, these data are displayed in comparison with the prevailing waste and water column concentrations in the NEA tests, and the results of other investigators in the field. Note that the accumulation levels in all species, including snails, in this study are well within the range of values observed in analagous organisms under field conditions in at least one coastal area (6). This does not imply that the observed As accumulation is or is not "acceptable." These tests and the available marine bioaccumulation literature are generally lacking in qualification of such factors as arsenic speciation, which can have an important impact on the ultimate toxicity of this chemical.

### Cadmium

Figures 10 (a-c) illustrate the Cd bioaccumulation results for this series of tests. Note that for all three test organisms in most of the exposure tanks there continued to be increasing bioaccumulation of Cd throughout the study. Figure 11 presents these data in comparison with the prevailing waste and water column concentrations, the 1978 data (from Part One of this report) and the results of other investigations.

FIGURE 7

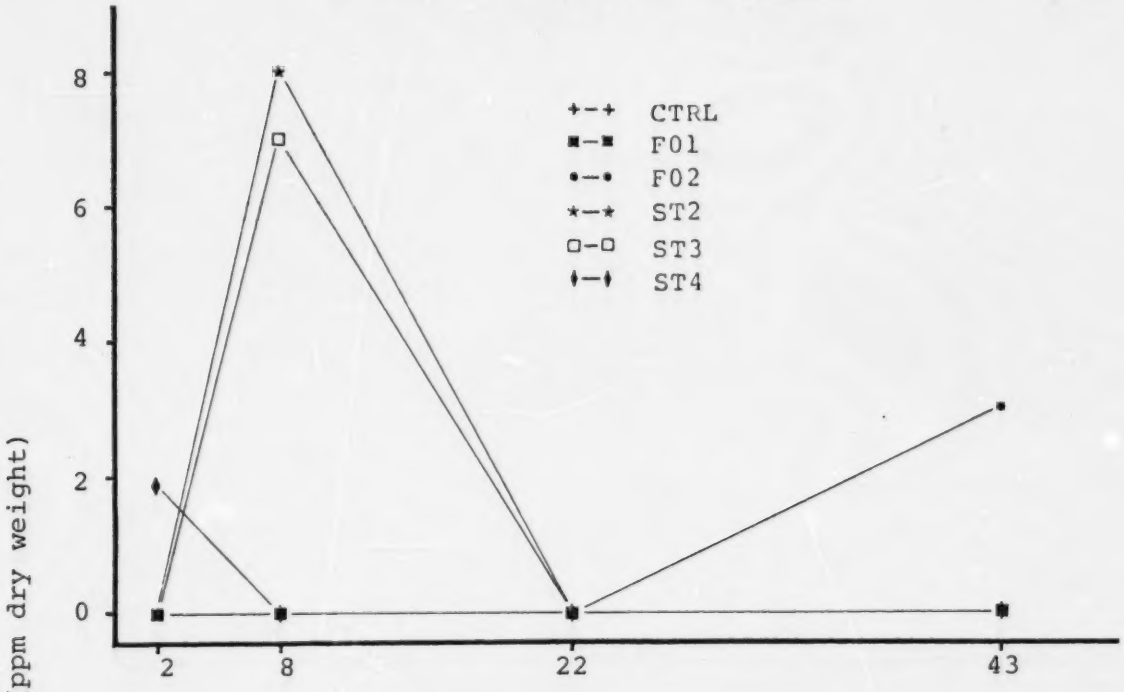
Arsenic Accumulation in Littorina




Source: New England Aquarium

FIGURE 8a

Arsenic Accumulation in Nereis



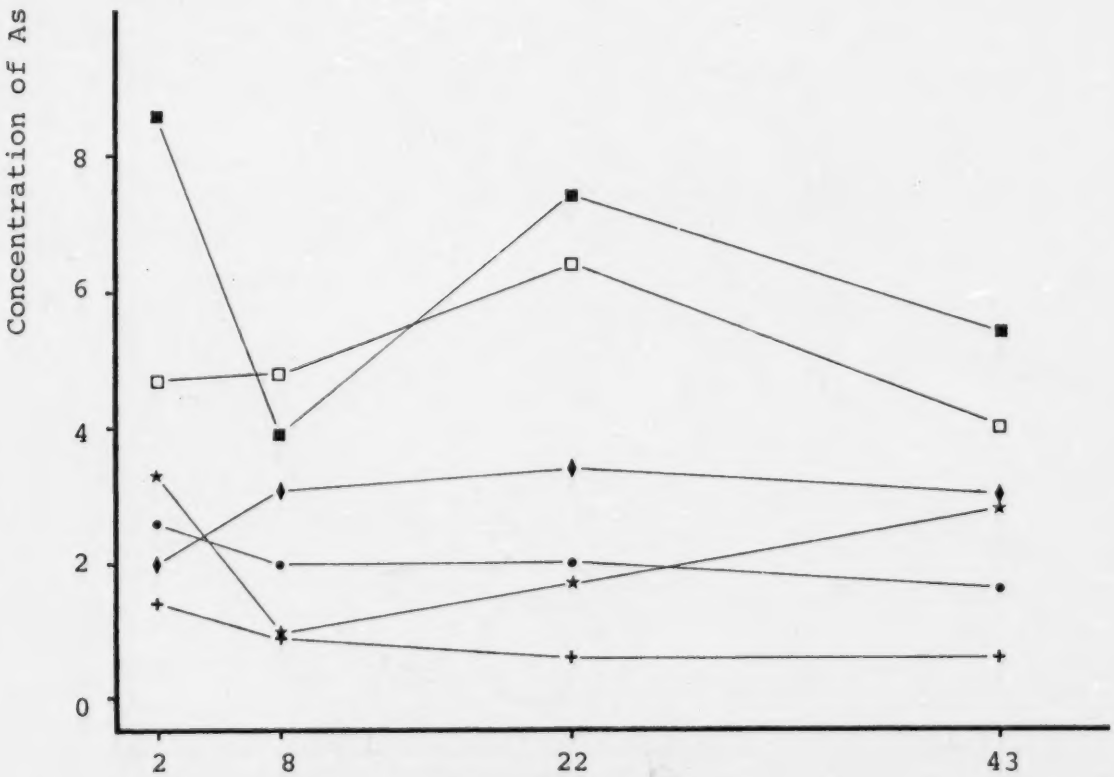




FIGURE 8b

Arsenic Accumulation in Mya

Source: New England Aquarium

Figure 9

Arsenic in Waste, Water Column and Organism Tissue

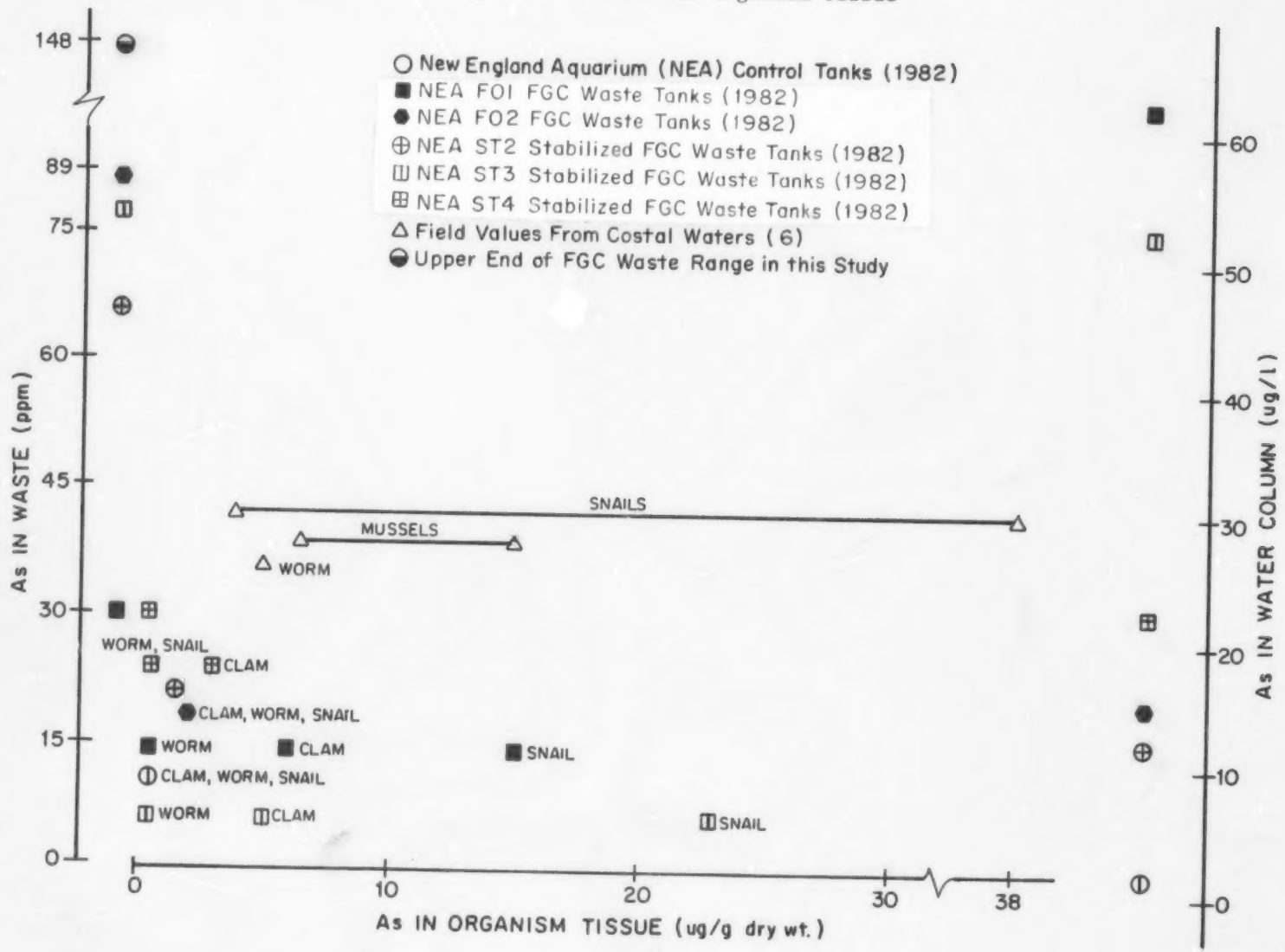
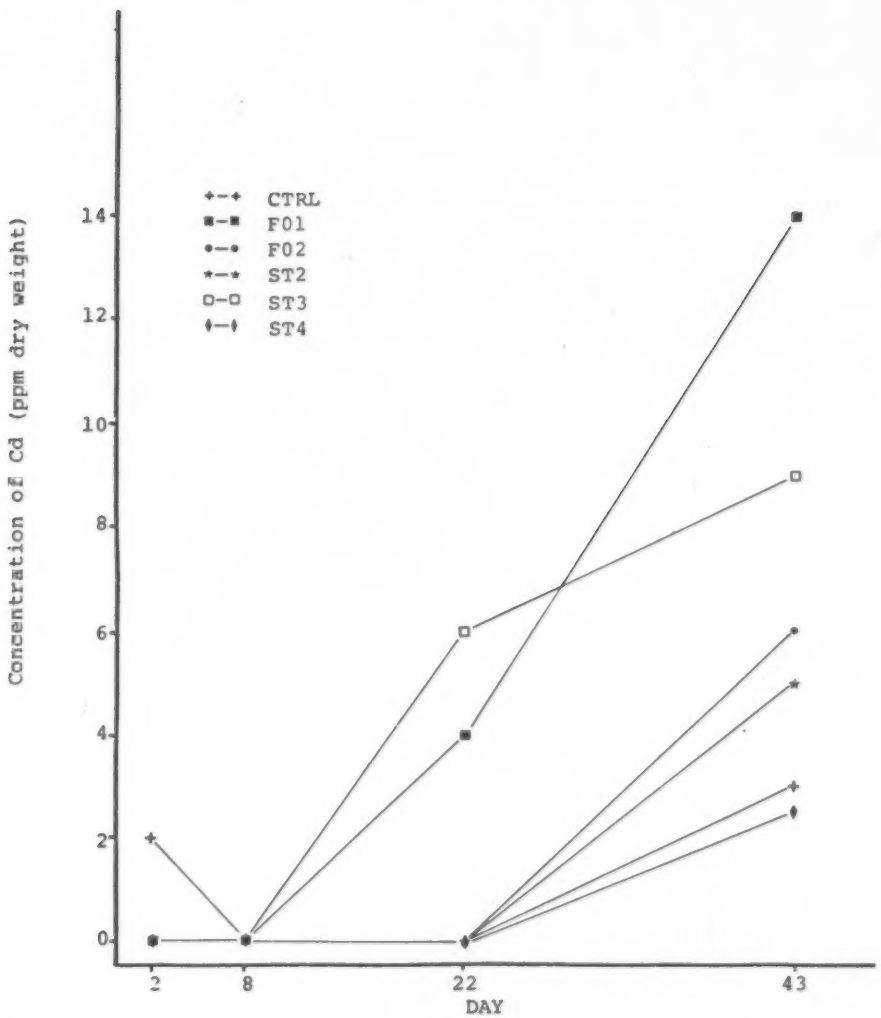


FIGURE 10a

Cadmium Accumulation in Littorina




Source: New England Aquarium

FIGURE 10b

Cadmium Accumulation in Nereis

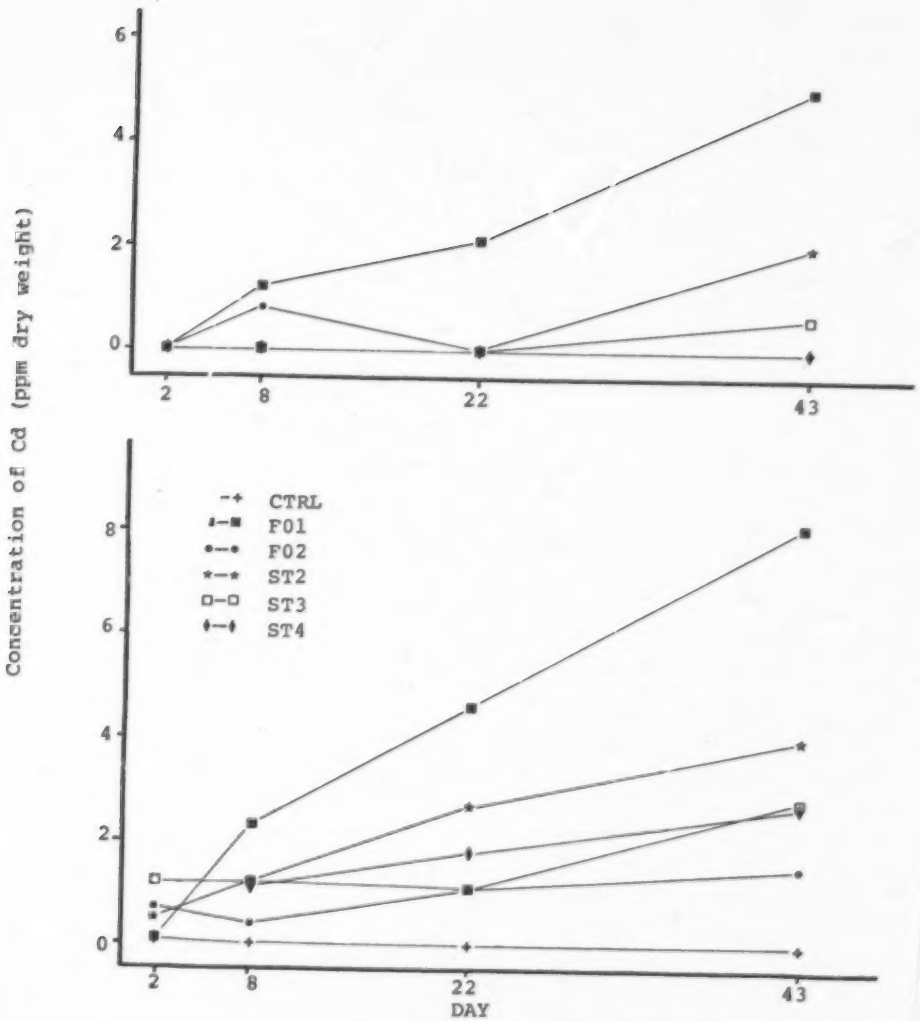


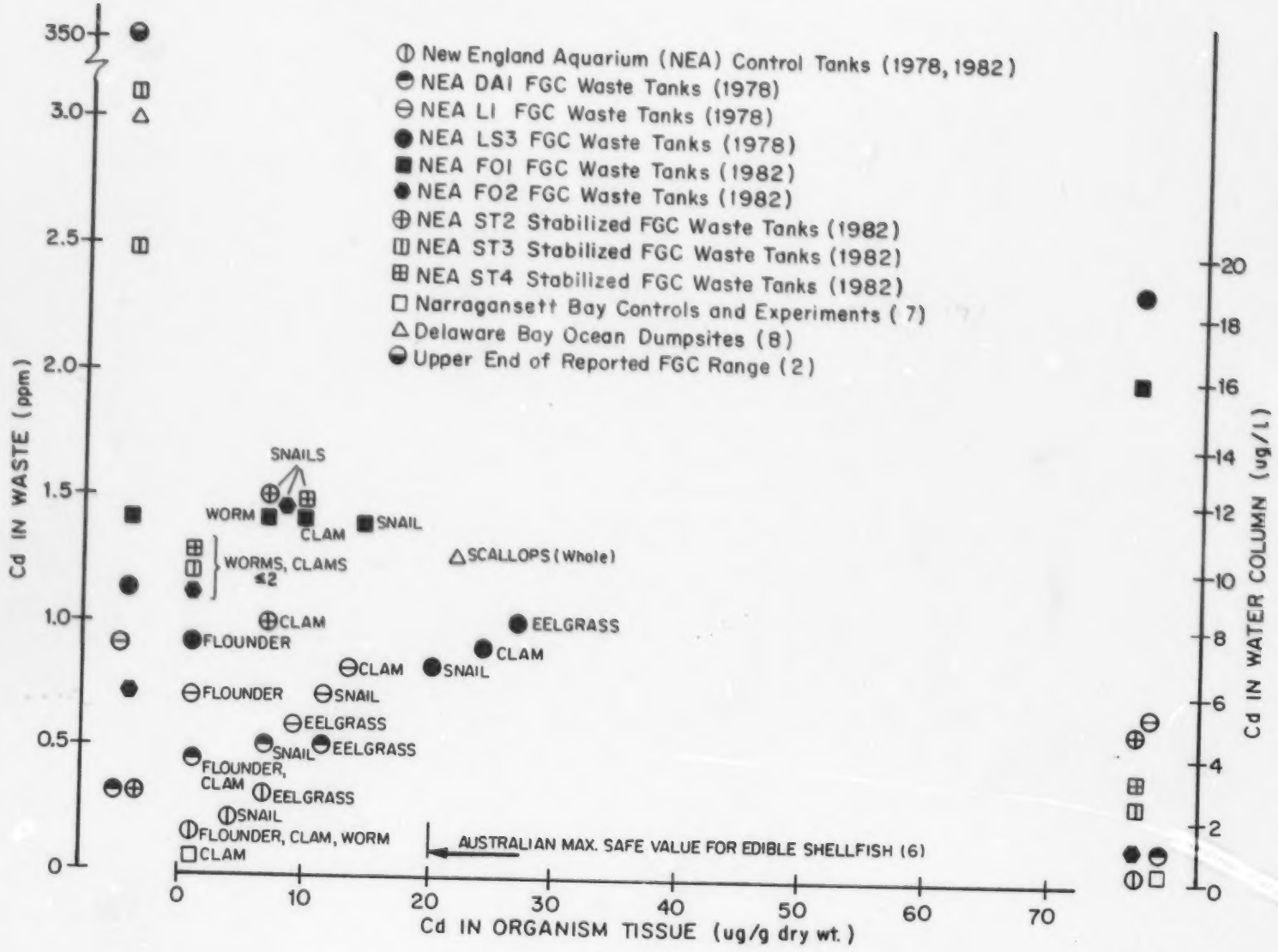

FIGURE 10c

Cadmium Accumulation in Mya

Source: New England Aquarium

Figure 11

Cadmium in Wastes, Water Column and Organism Tissue



Note that the values for the stabilized wastes are generally lower than for the unstabilized wastes, and that all the test results from this program generally reflect values comparable to those measured in shellfish at existing ocean dumping sites, and below or approaching a maximum safe value set for Cd in edible shellfish (6).

Chromium

Figures 12 (a-c) illustrate the data for Cr bioaccumulation from this series of tests. Note that increasing bioaccumulation generally prevailed at the conclusion of the test for each of the three species exposed to the forced oxidation wastes FO1, FO2 and ST4, both unstabilized and stabilized. Figure 13 illustrates these data in comparison with the prevailing levels of Cr in the test wastes and water column, and with the results of other investigations. Note that the release and bioaccumulation of $Cr^{+6}$ appears to have remained relatively unaffected by the FGC waste stabilization process used here to produce ST4. Further note that the Cr accumulation values obtained in these tests are comparable to other laboratory test results and to field values reported for the same types of organisms (6).

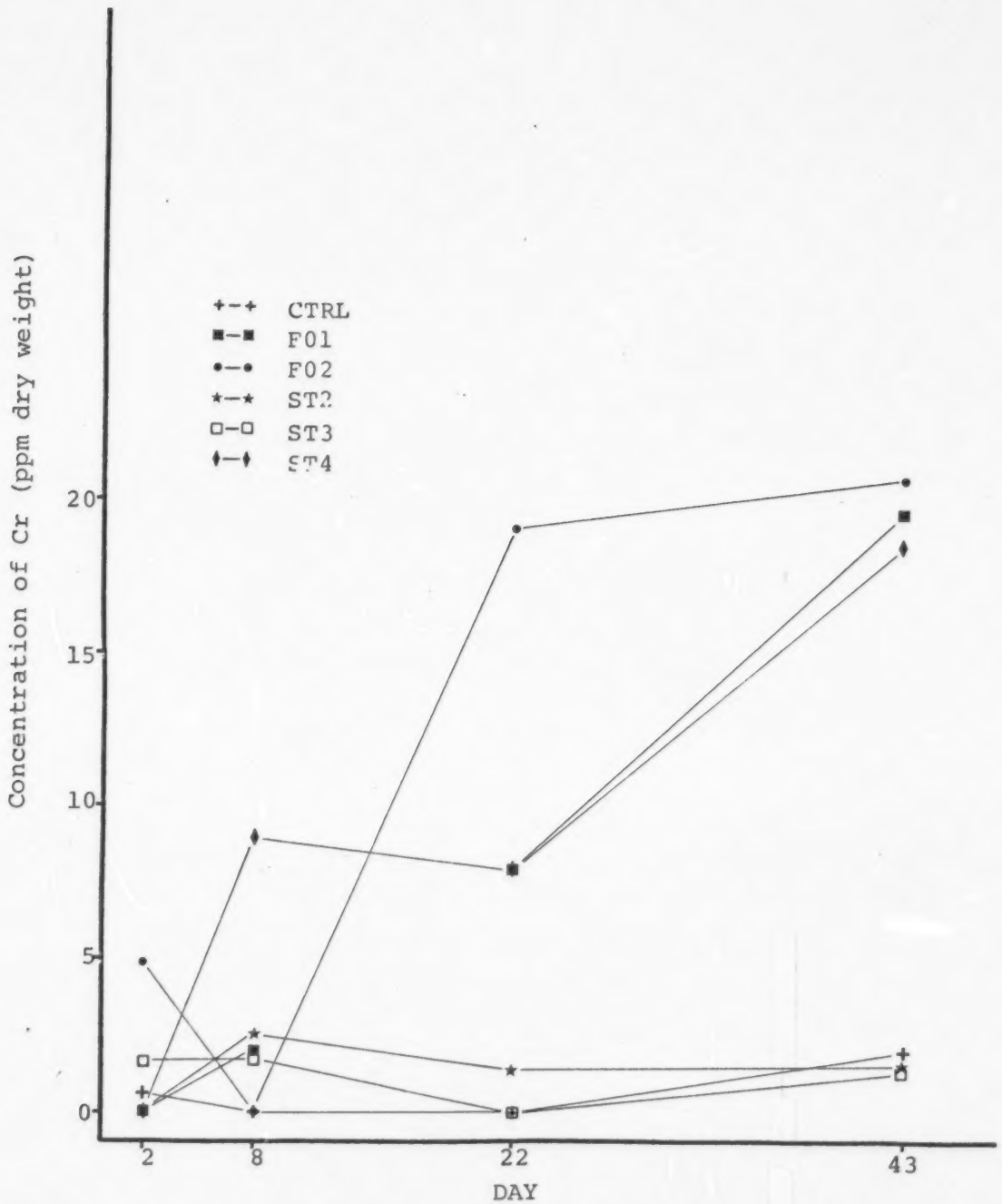
The referenced field values in the same range as those observed here were reported along with an assertion that the occasional high values of $Cr^{+6}$ in some edible shellfish have not served to inhibit continued harvest and consumption (6).

Selenium

Figures 14 (a-c) illustrate the Se bioaccumulation results for this series of tests. Note that the worms and snails generally accumulated little Se, and that accumulation appeared to peak in the middle of the experiment and decline thereafter. The data for clams in each of the FGC waste tanks indicate increasing Se accumulation with time, but still in the low ppm range. Figure 15 presents these data in comparison with the prevailing levels of Se in the test wastes and water columns, and the results of other investigations. Note that

FIGURE 12a

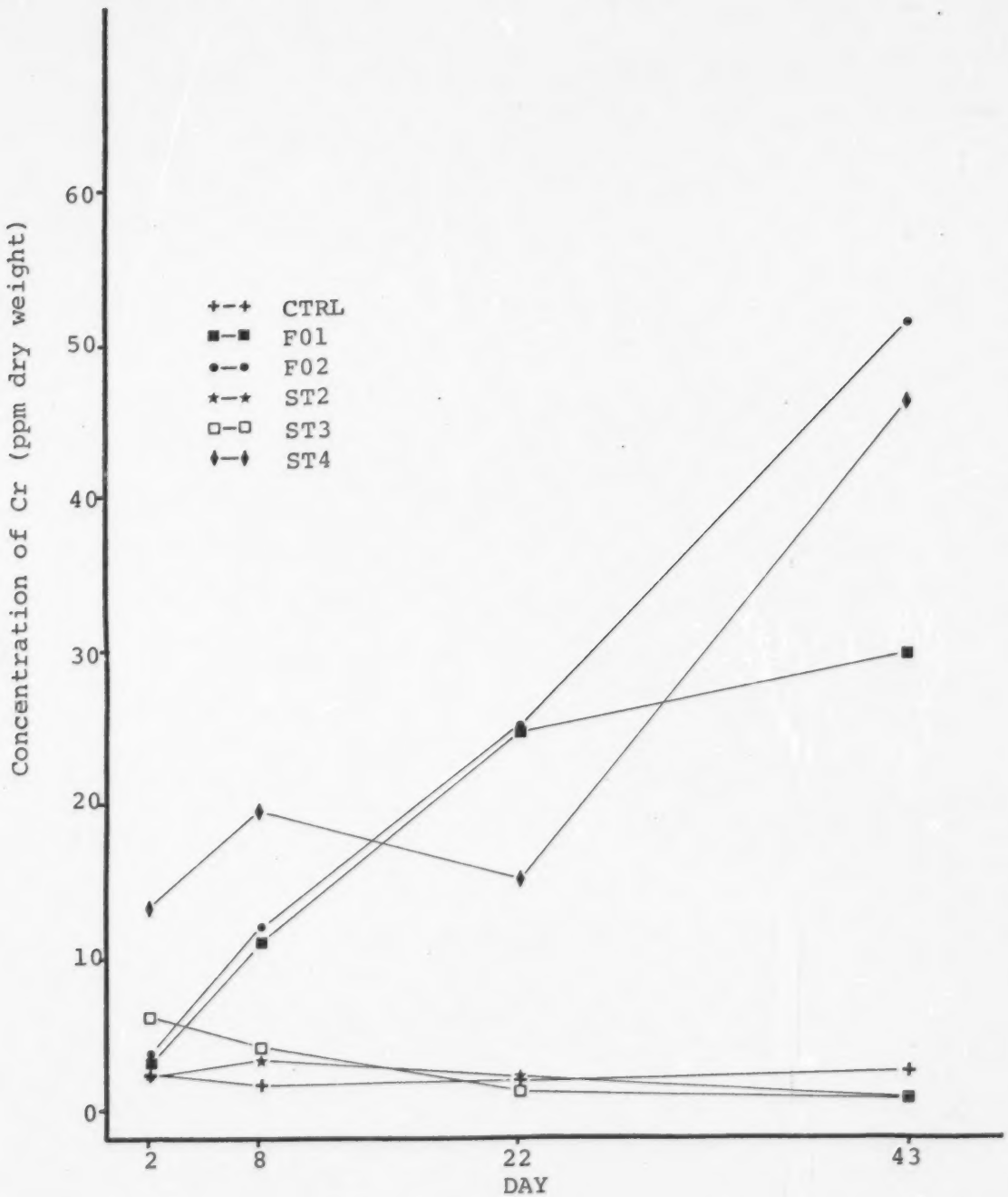
Chromium Accumulation in Littorina




Source: New England Aquarium

FIGURE 12b

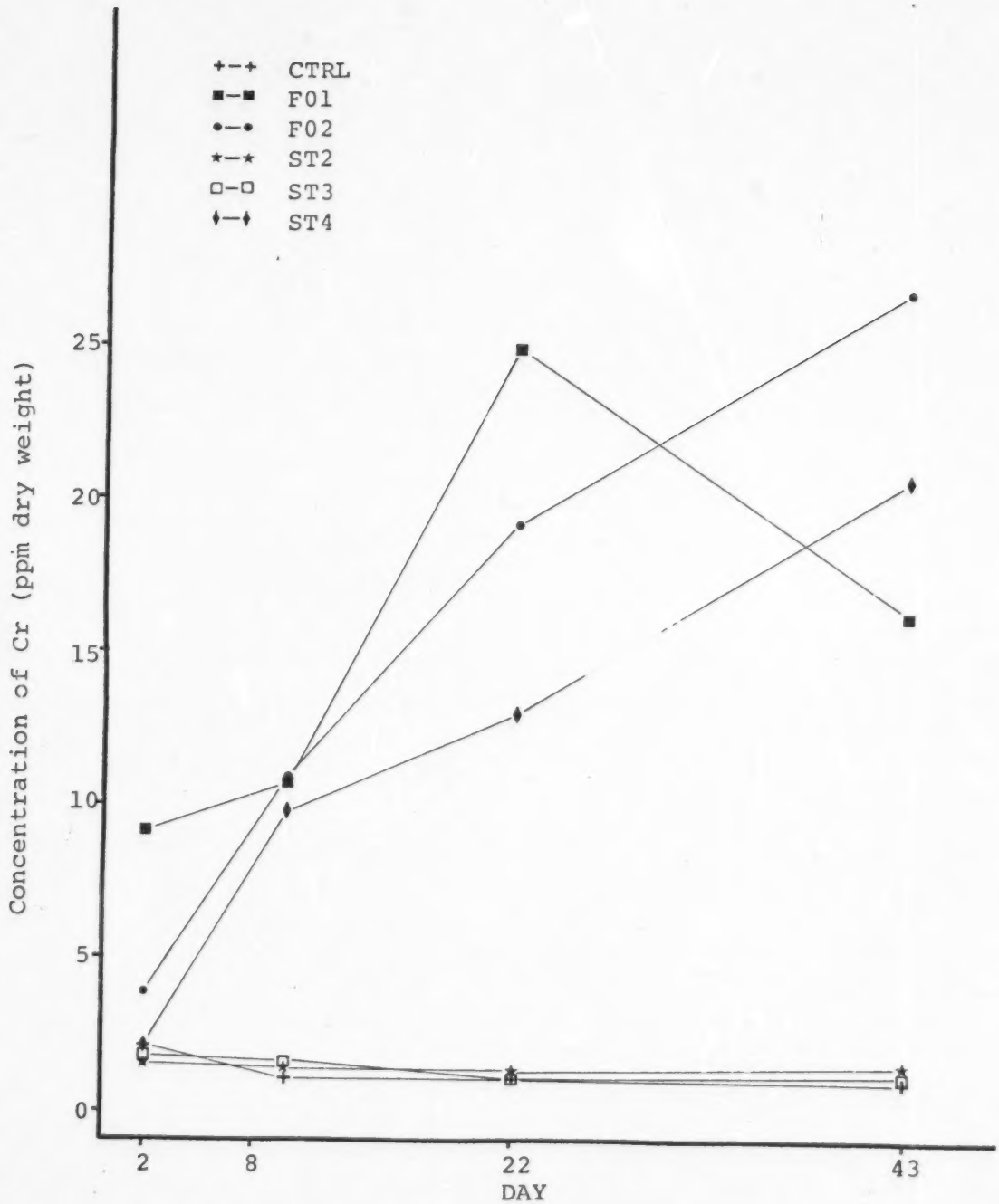
Chromium Accumulation in Nereis




Source: New England Aquarium

FIGURE.12c

Chromium Accumulation in Mya




Source: New England Aquarium

Figure 13

Chromium in Waste, Water Column and Organism Tissue

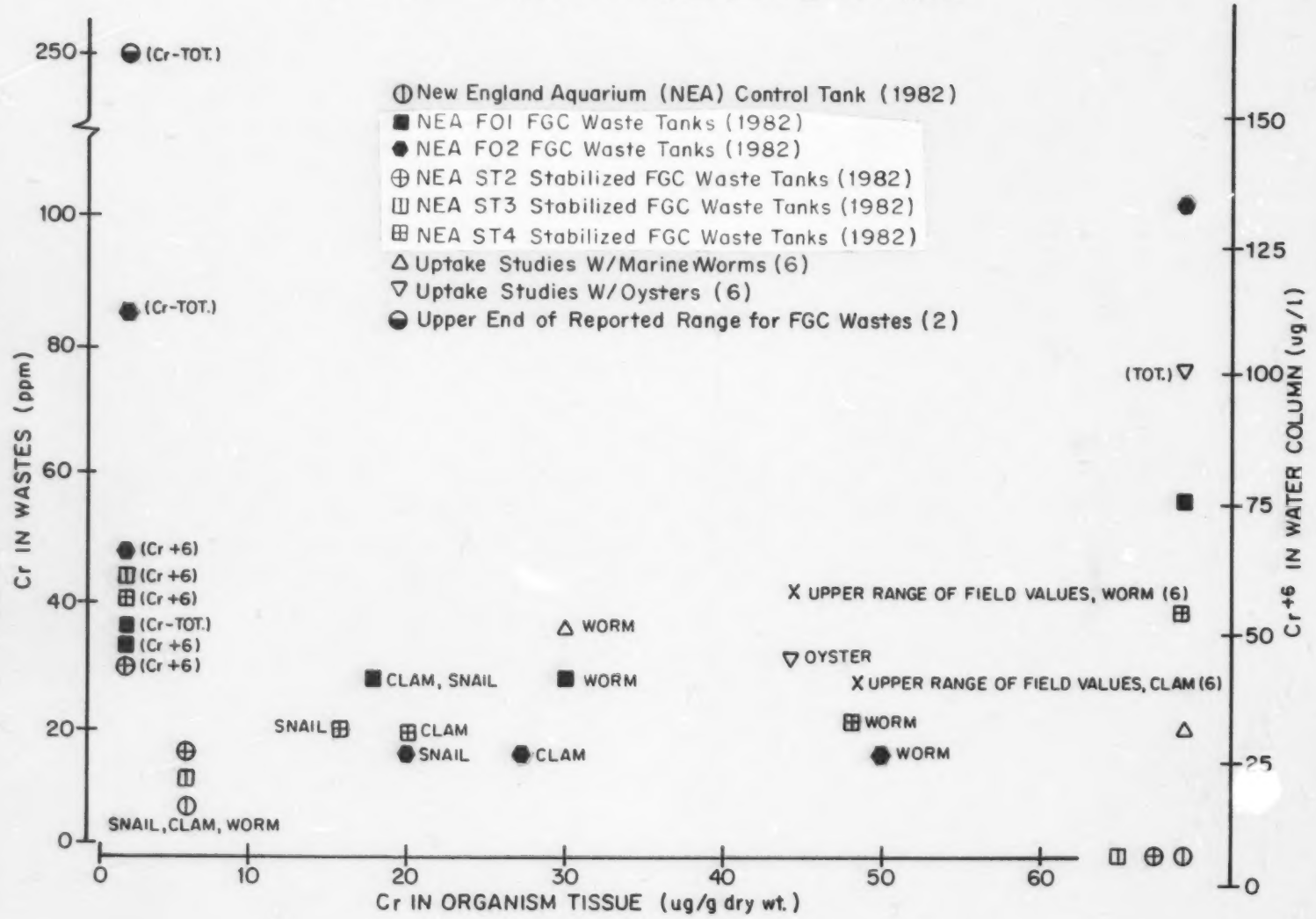
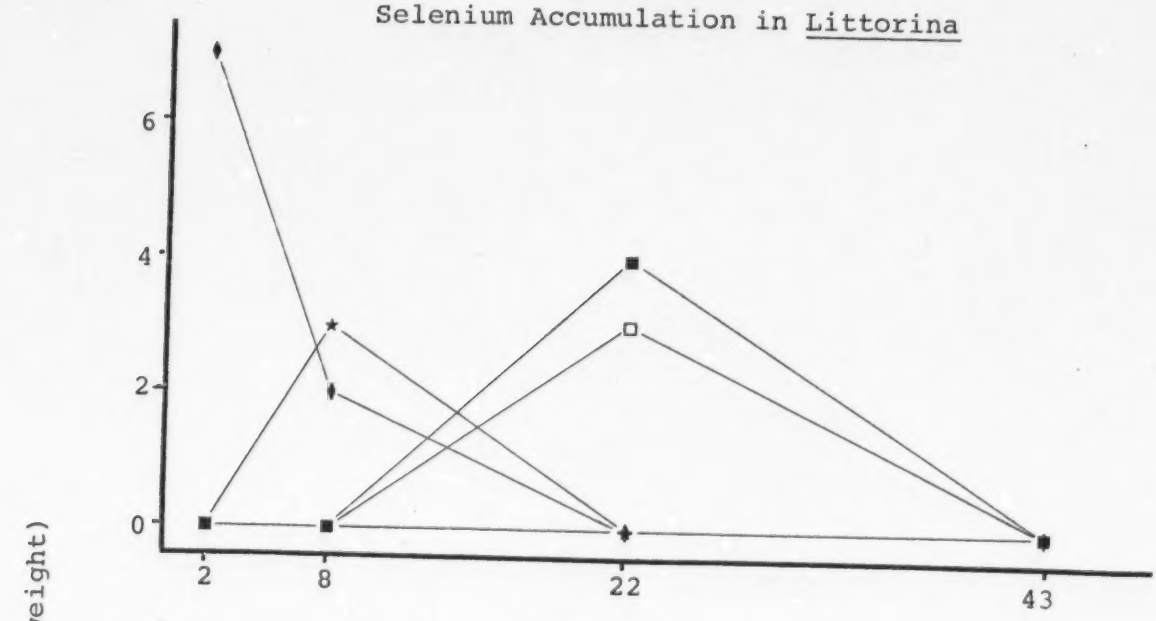


FIGURE 14a

Selenium Accumulation in Littorina



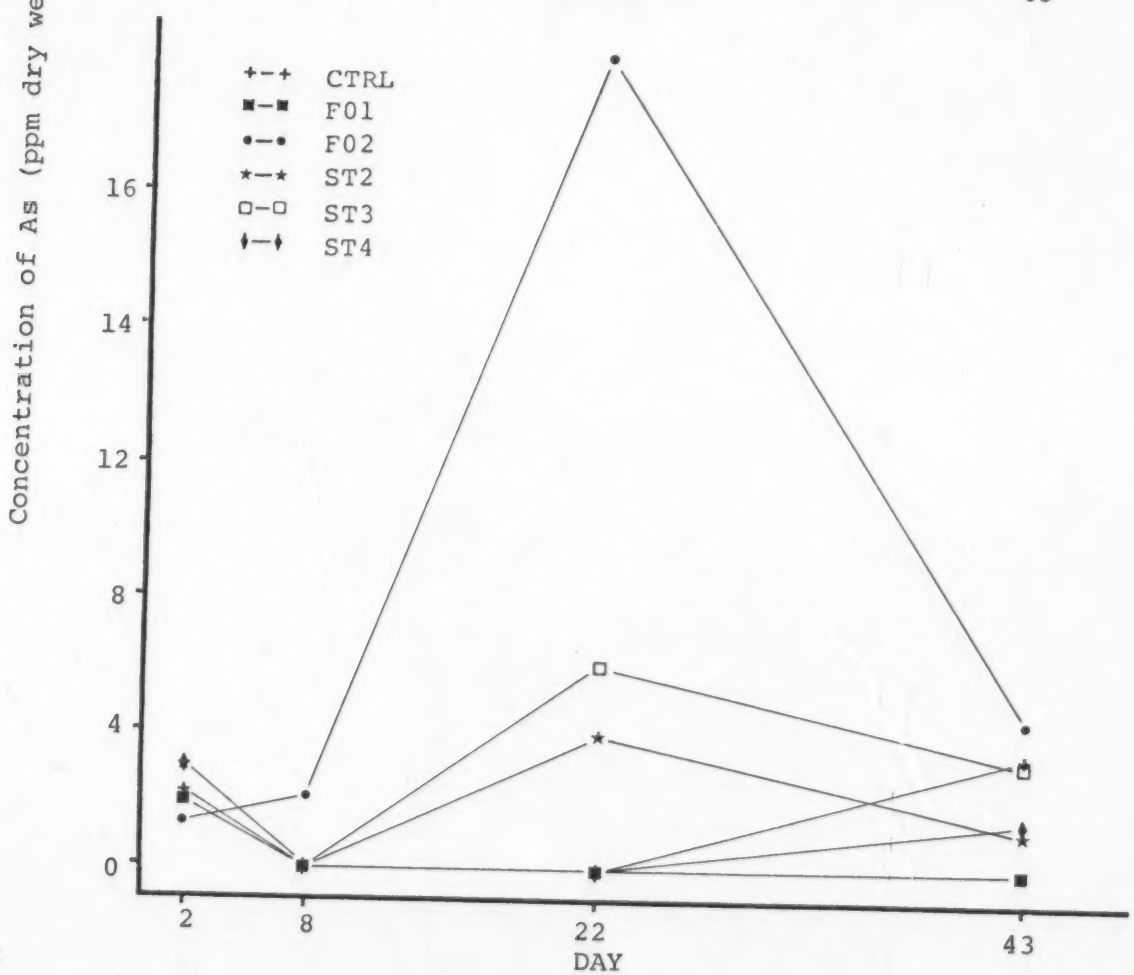



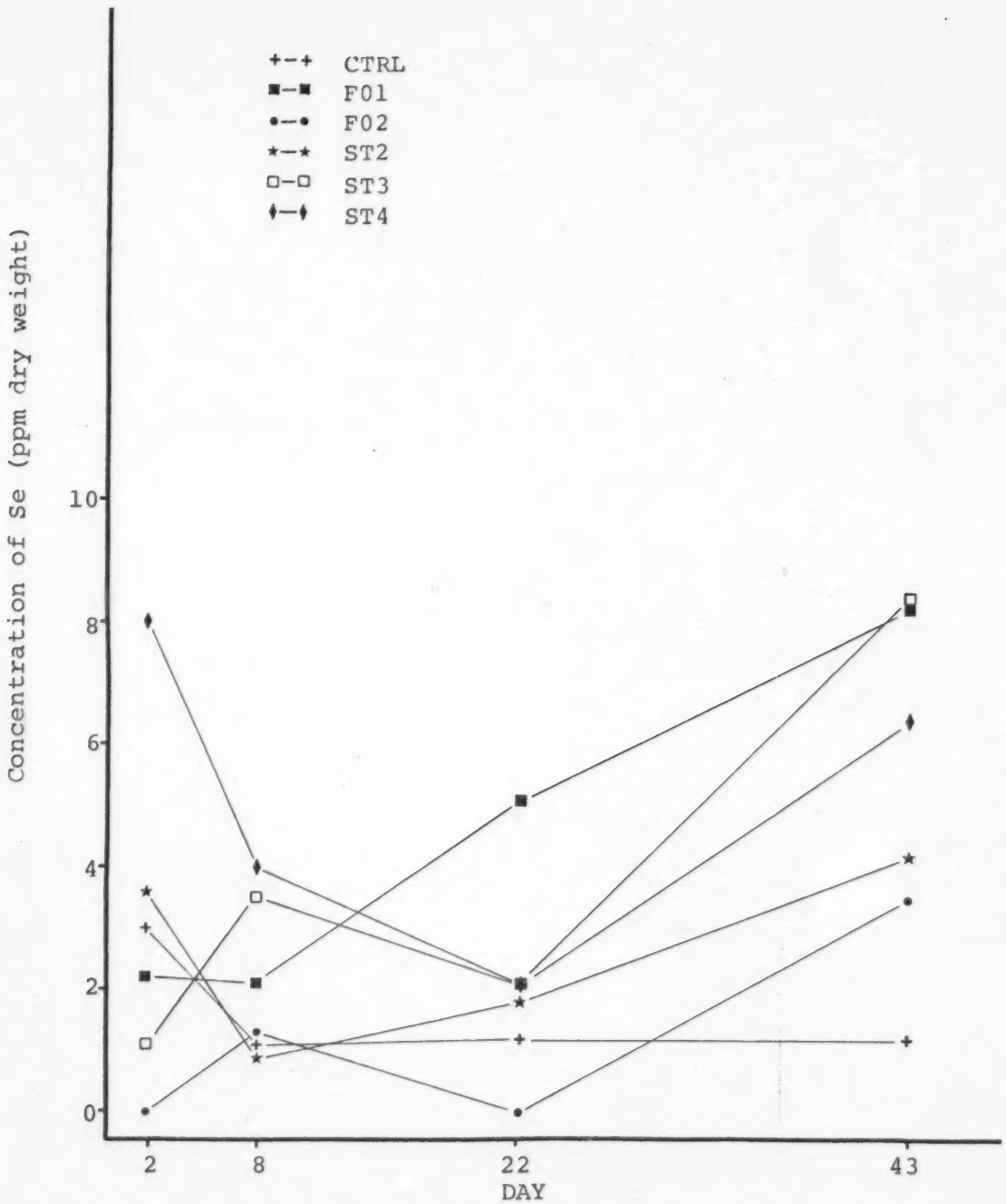

FIGURE 14b

Selenium Accumulation in Nereis

Source: New England Aquarium

FIGURE 14c

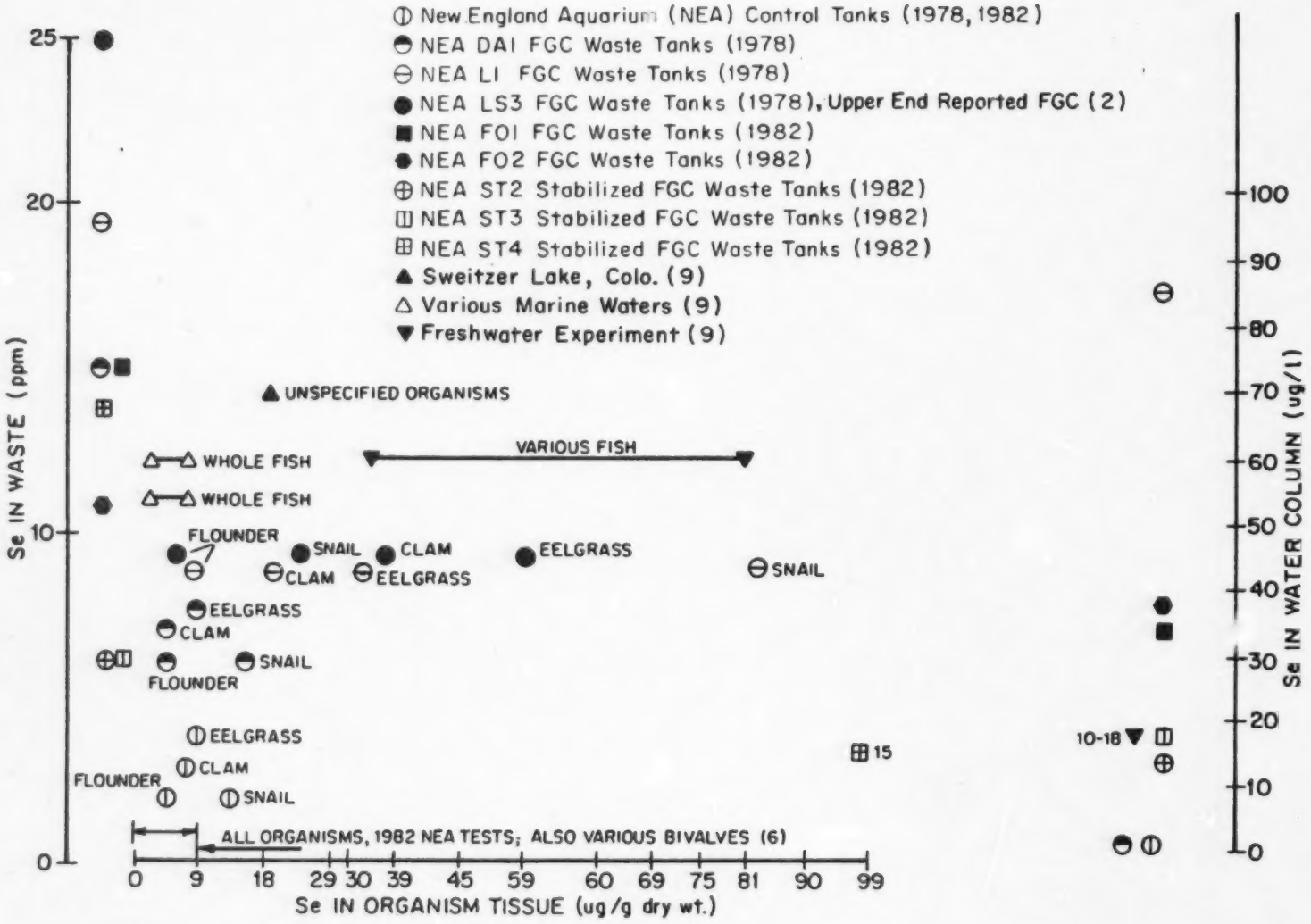
Selenium Accumulation in Mya




Source: New England Aquarium

Figure 15

Selenium in Wastes, Water Column and Organism Tissue




NOTE: DETECTION LIMIT VALUES USED AT 1/2 FACE VALUE (eg. <20=10)

levels in this series of tests were generally lower in all media than those reported in the Part One experiments. Note further that the values from the Part Two tests correspond very closely to the values reported by other investigators for similar organisms under various field and laboratory conditions (6)(9).

## V. SUMMARY EVALUATION OF ENVIRONMENTAL IMPACT POTENTIALS

Based on findings of the studies in this program (References 1 and 3 and both parts of this report) and the findings of the S.U.N.Y. C-WARP program (10,11,12), updated summary evaluations of potential environmental impacts of at-sea disposal of FGC wastes are presented below.

### A. Benthic Sedimentation Impacts

As discussed in Part One of this report, the physical suitability of soil-like FGC wastes as a benthic substrate remained an issue of potential concern for those conventional disposal situations on the continental shelf where the disposed wastes would not be subject to dispersal and admixing with local sediments. The S.U.N.Y. program results (10,11,12) documenting waste colonization at field scale suggest that such concern would not be applicable to brick-like, stabilized FGC wastes while they maintain their physical integrity. Likewise, the results of the NEA tank tests with both unstabilized and stabilized soil-like FGC wastes suggest that benthic marine organisms which would otherwise inhabit various or fine-grained natural substrates (e.g., the worms and clams in these tests) would not be limited by the physical characteristics of soil-like FGC waste substrates. However, as discussed in V.C. and D. below, the chemical characteristics of certain soil-like FGC wastes (i.e., their oxygen demand and/or trace metal leaching) may require mitigation even if the wastes are physically suitable as substrate in disposal areas with naturally occuring fine-grained sediments.

Like various dredged materials, fine-grained, soil-like FGC wastes would be expected to prove unsuitable substrates for indigenous organisms if concentrated on areas of the ocean bottom that would otherwise be covered by coarse sand and/or reef substrates.

Site selection and dispersed disposal, particular in well-mixed areas and in the deep ocean, appear to be reasonably sure means of avoiding potentially adverse physical benthic sedimentation impacts.

B. Suspended Sediment Impacts

Part Two of this study and the S.U.N.Y. program did not focus on any specific investigations of suspended sediment impacts of FGC waste disposal. One of the S.U.N.Y. experiments (12) did determine that an agitated, ground slurry of stabilized waste proved lethal to shellfish at a concentration of about 2 g/l. This result, however, does not reflect a condition to be expected in at-sea disposal of brick-like, stabilized FGC wastes.

The absence of observable acute toxicity in the Part Two studies with two additional sulfate-rich, unstabilized FGC wastes (FO1 and FO2) tends to suggest that the potential, if any, for these wastes to have adverse effects during descent in the water column would be restricted to uniquely contaminated wastes or samples, like the LS3 sample tested in Part One of the study.

There is presently no basis for revising any of the other observations on potential suspended sediment impacts as discussed in Section IV.B. of Part One of this report.

C. Sulfite-Related Oxygen Depletion

The field-scale observations of the S.U.N.Y. program (10,11,12) and the lab results of Part Two tend to confirm the observations in Part One of this report, i.e., that a combination of concentrated, soil-like, sulfite-rich FGC waste deposition and bio-turbation may be required to cause ecologically significant oxygen depletion. The investigations of oxygen depletion by stabilized wastes in Part Two of this study indicated that such depletion would occur with stabilized, sulfite-rich wastes, but to a lesser degree and at a slower rate than for the unstabilized wastes studied previously. These observations reinforce

the Part One finding that a combination of dispersed disposal and voluntary avoidance by site finfish may be an acceptable means of avoiding sulfite-related toxicity due to oxygen depletion by FGC wastes.

D. Trace Contaminant Impacts

The results of the leaching and biological exposure testing in Part Two of the study tend to confirm for additional stabilized and unstabilized FGC wastes the Part One findings for nickel and zinc, and to suggest similar findings for copper. For all three of these metals, the combined lack of significant incremental leaching from the tested wastes resulted in incremental changes in ambient seawater concentrations below the levels reported to cause adverse ecological effects in the marine environment. Because of the nature of the observed leaching and bioaccumulation trends, and because the tested wastes are relatively high in concentrations of the three chemicals (compared to the reported range for FGC wastes), it appears unlikely that any of these metals would prove a limiting factor in considerations of FGC waste disposal at-sea.

The Part Two results with two similar wastes tend to reinforce the hypothesis that the toxic trace contamination of the LS3 waste sample used in Part One was a relatively unique phenomenon. This suggests that such contamination should not broadly anticipated by those considering ocean disposal of unstabilized, sulfate-rich FGC wastes, and that the required standard EPA ocean disposal program bioassays could be used to screen any such contaminated wastes prior to disposal.

Results for other trace metals, notably arsenic, cadmium, chromium and selenium and inconclusive. The absence of toxicity and the extent of bioaccumulation in the Part Two tests suggest that relatively short-term exposures would be environmentally acceptable, but leave open some questions about the impacts of prolonged exposure. In particular, because the concentrations of these elements were continuing to rise in one or more test species at the conclusion of the

Part Two thirty-day exposure tests, tests of longer duration under equally or more representative mixing conditions (preferably at field scale) would be required to determine the impact potential of FGC wastes high in leachable concentrations of these elements.

## VI. CONCLUSIONS

The two overall conclusions of the earlier assessments (1,3) are still considered valid. These conclusions, which emphasize the need for case-by-case analyses of prospective at-sea disposal of FGC wastes, and affirm the technical feasibility of four available control options, are contained in their entirety in Section II of Part One of this report. More specific conclusions based on the results and assessment described in Part Two of this report are as follows:

- The ocean disposal of stabilized, sulfite-rich FGC waste appears to be environmentally preferable from the standpoint of sulfite-related oxygen depletion. Chemical and bioassay testing of such wastes in this program revealed lesser oxygen depletion phenomena than those observed in previous tests with unstabilized sulfite-rich FGC wastes. Mitigation of this impact potential by dispersed disposal may be feasible and necessary, but requires field-scale investigation.

- The previously observed incidence of contamination-related acute or sub-chronic toxicity associated with one sample of a sulfate-rich, unstabilized FGC wastes appears to have been highly waste-specific (possibly sample-specific). Such toxicity should not be expected for a broad spectrum of sulfate-rich FGC wastes, and can be evaluated on a case-by-case basis with required, standard ocean disposal bioassays.

- The limited potential for near-term release and accumulation of copper, nickel and zinc from either unstabilized or stabilized FGC wastes appears unlikely to constrain at-sea disposal of these wastes.

- The absence of apparent toxicity and the levels of bioaccumulation evident from exposure of marine organisms to combinations of the other principal trace metals in FGC waste leachates (e.g., As, Se, Cd and Cr) suggest that relatively

short-term exposures would be environmentally acceptable, but leave open some questions about the impacts of prolonged exposure. Determinations of ultimate impact potential for wastes high in these elements should be made upon completion of studies of longer duration under representative exposure conditions, preferably at field scale.

- FGC waste stabilization by addition of lime and fly ash appears to be a potentially effective means of mitigating impacts associated with the release of some trace metals (e.g., cadmium) but not others (e.g., Se, Cr).

- Disposal options which continue to appear promising and are recommended for further research include:

  - dispersed disposal of all forms of FGC wastes on the continental shelf or in the deep ocean;

  - conventional or concentrated disposal of stabilized FGC wastes on the continental shelf or in the deep ocean; and

  - conventional or concentrated disposal of unstabilized, sulfate-rich FGC wastes in the deep ocean.

## VII. RECOMMENDATIONS FOR ADDITIONAL RESEARCH

The following research needs were identified on the basis of the investigations described in Part Two of this report:

- Limited field-scale tests with sulfite and metal-rich FGC wastes should be conducted to investigate the importance of:

  1. avoidance responses as potentially mitigative of the sulfite-related toxicity of sulfite-rich FGC wastes; and

  2. longer-term chronic uptake and toxicity of As, Cd, Cr and Se leached from FGC wastes under representative conditions for leaching and water exchange.

- Investigation of any field situations where FGC wastes have entered or been placed in marine environments should be encouraged.

## VIII. REFERENCES


1. Lunt, R.R., C.B. Cooper, S.L. Johnson, J.E. Oberholtzer, G.R. Shimke, and W.I. Watson, "An Evaluation of the Disposal of Flue Gas Desulfurization Wastes in Mines and the Ocean: Initial Assessment," EPA 600/7-77-051, U.S. Environmental Protection Agency, Office of Research and Development, 1977.

2. Santhanam, C.J., R.R. Lunt, C.B. Cooper, D.E. Kleinschmidt, I. Bodek, and W.A. Tucker (Arthur D. Little, Inc.), and C.R. Ullrich (University of Louisville), "Waste and Water Management for Conventional Coal Combustion, Assessment Report - 1979," EPA 600/7-80-012, U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, North Carolina, 1980.

3. Lunt, R.R., C.B. Cooper, A.S. Reyman, S.L. Johnson, I. Bodek, W.I. Watson (Arthur D. Little, Inc.) and G.C. McLeod, A.J. Barker (Edgerton Research Laboratory, New England Aquarium), "An Evaluation of the Disposal of Flue Gas Desulfurization Wastes in Coal Mines and At-Sea: Refined Assessment," U.S. Environmental Protection Agency, Office of Research and Development, Contract No. 68-03-2334, 1981.

4. Federal Register, Volume 44, No. 52, March 15, 1979.

5. Eisler, Ronald and Raymond J. Hennekey, "Acute Toxicities of $Cd^{2+}$, $Cr^{+6}$, $Hg^{2+}$, $Ni^{2+}$ and $Zn^{+2}$ to Estuarine Macrofauna," EPA-600/J-77-151, U.S. Environmental Protection Agency, Environmental Research Laboratory, Narragansett, Rhode Island, 1977.

6. Eisler, Ronald, Trace Metal Concentrations in Marine Organisms, Pergamon Press, 1981.

7. Eisler, Ronald and Raymond J. Hennekey, "Toxicity Evaluation of a Complex Metal Mixture to the Soft Shell Clam (Mya arenaria)," EPA-600/J-77-149, U.S. Environmental Protection Agency, Environmental Research Laboratory, Narragansett, Rhode Island, 1977.

8. Reynolds, Bruce H., "Trace Metals Monitoring at Two Ocean Disposal Sites," EPA-600/3-79-037, U.S. Environmental Protection Agency, Environmental Research Laboratory, Narragansett, Rhode Island, 1979.

9. Birkner, John H., "Selenium in Aquatic Organisms from Seleniferous Habitats," AFIT Report No. Ci-79-34D, Defense Documentation Center, Defense Logistics Agency, Cameron Station, Alexandria, Virginia, 1978.

10. State University of New York, Stony Brook, NY and I.U. Conversion Systems, Inc. "Draft Report, Coal Waste Artificial Reef Program, C-WARP," submitted to New York State Energy Research and Development Authority, Albany, NY, March 6, 1979.

11. Marine Sciences Research Center, State University of New York, "Coal Waste Artificial Reef Program, Phase 3, Volume 1: Summary Report," EPRI CS-2009, Volume 1, Project 1341-1, Interim Report for Electric Power Research Institute, Palo Alto, California, October 1981.

12. Marine Sciences Research Center, State University of New York, "Coal Waste Artificial Reef Program, Phase 4A," EPRI CS-2574, Project 1341-1, prepared for New York State Energy Research and Development Authority, Albany, New York, Interim Report - Electric Power Research Institute, Palo Alto, California, September 1982.